The update of the line positions and intensities in the line list of carbon dioxide for the HITRAN2020 spectroscopic database

E.V. Karlovets, I.E. Gordon, L.S. Rothman, R. Hashemi, R.J. Hargreaves, G.C. Toon, A. Campargue, V.I. Perevalov, P. Čermák, M. Birk, et al.

To cite this version:

E.V. Karlovets, I.E. Gordon, L.S. Rothman, R. Hashemi, R.J. Hargreaves, et al.. The update of the line positions and intensities in the line list of carbon dioxide for the HITRAN2020 spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer, 2021, 276, pp.107896. 10.1016/j.jqsrt.2021.107896 . hal-03433127

HAL Id: hal-03433127
https://hal.science/hal-03433127
Submitted on 17 Nov 2021

Journal of Quantitative Spectroscopy and Radiative Transfer

The update of the line positions and intensities in the line list of carbon dioxide for the HITRAN2020 spectroscopic database

--Manuscript Draft--

Manuscript Number:	
Article Type:	VSI:HITRAN2020
Keywords:	Carbon dioxide; CO2 line lists; HITRAN database; HITRAN2020; spectroscopic line parameters
Corresponding Author:	Ekaterina Karlovets Harvard-Smithsonian Center for Astrophysics Cambridge, MA United States
First Author:	E.V. Karlovets
Order of Authors:	E.V. Karlovets
	I.E. Gordon
	L.S. Rothman
	R. Hashemi
	R.J. Hargreaves
	G.C. Toon
	A. Campargue
	V.I. Perevalov
	P. Čermák
	M. Birk
	G. Wagner
	J.T. Hodges
	J. Tennyson
	S.N. Yurchenko
Abstract:	This paper describes the updates of the line positions and intensities for the carbon dioxide transitions in the 2020 edition of the HITRAN spectroscopic database. The new line list for all 12 naturally abundant isotopologues of carbon dioxide replaces the previous one from the HITRAN2016 edition. This update is primarily motivated by several issues related to deficient HITRAN2016 line positions and intensities that have been identified from laboratory and atmospheric spectra. Critical validation tests for the spectroscopic data were carried out to find problems caused by inaccuracies in CO2 line parameters. New sources of data were selected for the bands that were deemed problematic in the HITRAN2016 edition. Extra care was taken to retain the consistency in the data sources within the bands. The comparisons with the existing theoretical and semi-empirical databases (including ExoMol, NASA Ames, and CDSD-296) and with available experimental works were carried out. The HITRAN2020 database has been extended by including additional CO2 bands above 8000 cm-1, and magnetic dipole lines of CO2 were introduced in HITRAN for the first time by including the v2+v3 band in the 3.3-μm region. Although the main topic of this article are line positions and intensities, for consistency a recent algorithm for the line-shape parameters proposed in Hashemi et al. JQSRT (2020) was reapplied (after minor revisions) to the line list.
Suggested Reviewers:	Yan Tan tanyan@ustc.edu.cn
	Livio Gianfrani livio.gianfrani@unicampania.it
	Keyoon Sung

	Keeyoon.Sung@jpl.nasa.gov

Highlights

- The new HITRAN2020 line list for all 12 naturally abundant isotopologues of carbon dioxide replaces the previous one from the HITRAN2016 edition;
- Evaluation of the HITRAN CO_2 line lists by comparison to laboratory and atmospheric spectra below 8310 cm^{-1} was carried out;
- The updates made for the bands having mixed CDSD and UCL-IAO line intensities in the HITRAN2016 line list below 8000 cm^{-1} are presented;
- The CO_2 bands in the (1.4-2.1) µm region were improved;
- New CO_2 bands above 8000 cm^{-1} were added to the HITRAN2020 edition from the new high-temperature UCL-4000 $^{12}C^{16}O_2$ line list (ExoMol database) and the CRDS spectra for the $^{16}O^{12}C^{18}O$ isotopologue;
- The magnetic dipole 01111-00001 band of the $^{12}C^{16}O_2$ isotopologue in the 3.3 µm region was introduced into HITRAN for the first time;

The update of the line positions and intensities in the line list of carbon dioxide for the HITRAN2020 spectroscopic database

E.V.Karlovets [1,2*], I.E.Gordon [1*], L.S.Rothman[1], R. Hashemi [1], R.J.Hargreaves[1], G.C. Toon[3], A.Campargue[4], V.I. Perevalov[5], P. Čermák[6], M.Birk[7], G.Wagner[7], J.T.Hodges[8], J. Tennyson[9], and S.N.Yurchenko[9]

[1] Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, 60 Garden St, Cambridge, MA, USA
[2] Tomsk State University, Laboratory of Quantum Mechanics of Molecules and Radiative Processes, 36, Lenin Avenue, 634050, Tomsk, Russia
[3] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA
[4] University of Grenoble Alpes, CNRS UMR 5588, LIPhy, Grenoble F-38000, France
[5] V.E. Zuev Institute of Atmospheric Optics, 1, Academician Zuev square, 634055 Tomsk, Russia
[6] Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, 842 48 Bratislava, Slovakia
[7] Remote Sensing Technology Institute, German Aerospace Center (DLR), D-82234 Wessling, Germany
[8] National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
[9] Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, UK

Number of pages: 44 20 May 2021

Number of tables: 2

Number of figures: 17

Key words: Carbon dioxide; CO_2 line lists; HITRAN; spectroscopic line parameters.

* Corresponding author:
E-mails: ekarlovets@gmail.com (E.V.Karlovets), igordon@cfa.harvard.edu (I.E.Gordon)

Abstract

This paper describes the updates of the line positions and intensities for the carbon dioxide transitions in the 2020 edition of the HITRAN spectroscopic database. The new line list for all 12 naturally abundant isotopologues of carbon dioxide replaces the previous one from the HITRAN2016 edition. This update is primarily motivated by several issues related to deficient HITRAN2016 line positions and intensities that have been identified from laboratory and atmospheric spectra. Critical validation tests for the spectroscopic data were carried out to find problems caused by inaccuracies in CO_2 line parameters. New sources of data were selected for the bands that were deemed problematic in the HITRAN2016 edition. Extra care was taken to retain the consistency in the data sources within the bands. The comparisons with the existing theoretical and semi-empirical databases (including ExoMol, NASA Ames, and CDSD-296) and with available experimental works were carried out. The HITRAN2020 database has been extended by including additional CO_2 bands above 8000 cm^{-1}, and magnetic dipole lines of CO_2 were introduced in HITRAN for the first time by including the $\nu_2+\nu_3$ band in the 3.3-μm region. Although the main topic of this article are line positions and intensities, for consistency a recent algorithm for the line-shape parameters proposed in Hashemi et al. JQSRT (2020) was reapplied (after minor revisions) to the line list.

1. Introduction

A plethora of critical applications drives a constant demand for ever higher-quality spectroscopic parameters of carbon dioxide (CO_2) transitions. Atmospheric CO_2 is the key gaseous contributor to the greenhouse effect in the terrestrial atmosphere. Its continuous increase in the atmosphere over the last two centuries from anthropogenic sources is considered the principal driver of climate change. The Martian and Venusian (and those of many rocky exoplanets) atmospheres consist mostly of carbon dioxide with mole fractions of over 95%. Monitoring CO_2 is important in combustion. Currently, there are several satellite-based observatories, including GOSAT[1–3] , GOSAT-2 [4] , OCO-2 [5,6] , OCO-3 [7], MIPAS [8], and ACE [9] as well as ground-based networks TCCON [10] and NDACC [11], monitoring atmospheric CO_2. Accurate interpretation of the data from these missions is necessary to make informed decisions regarding controlling of the anthropogenic contribution to the greenhouse effect and ultimately the climate change. All aforementioned CO_2 remote sensing activities depend on the reliability of the reference CO_2 spectroscopy.

The HITRAN molecular spectroscopic database is the widely recognized standard providing the spectroscopic data for atmospheric applications. Among many other molecules, it includes the necessary calculated and experimental parameters for all naturally abundant isotopologues of carbon dioxide. The HITRAN2016 [12] CO_2 line list for 12 stable isotopologues contains 559874 transitions. Most of the issues related to spectral completeness (at least below 8000 cm^{-1}) and insufficient accuracy of line parameters were resolved in HITRAN2016 [12]. However, there is still a lot of room for improvement to meet the ever-increasing demands of the scientific community. Since the release of the HITRAN2016 database[12] ,many new experimental and theoretical data have become available, and they can be used as sources for improving line positions, line intensities, and line-shape parameters of CO_2. The HITRAN-related updates, including the CO_2-air and CO_2-CO_2 line-shape parameters together with the speed dependence of the broadening parameters, their temperature-dependent exponents, the full and first-order line mixing as well as their temperature dependencies have been published in Hashemi et al. [13].

In the present work, we will mainly focus on the issues associated with deficiencies in line positions and intensities in HITRAN2016. Most of these problematic cases have been identified in new laboratory and atmospheric spectra, mainly from the Kitt Peak National Observatory, MkIV balloon, cavity ring down spectroscopy (CRDS) measurements, and the Total Carbon Column Observing Network (TCCON) [10,14–16]. A general review of the CO_2 bands affected by these issues was performed and alternative sources of data for each CO_2 problematic band were considered. Apart from new experimental data, the additional resources for improvements were provided by two recent comprehensive CO_2 line lists, namely the 2019 version of the semi-empirical CDSD-296 [17] list and the ExoMol variational nuclear motion line list [18], hereafter referred to as UCL-4000 Using these spectroscopic data, we improved and extended the CO_2 line lists for all 12 stable isotopologues of carbon dioxide.

The updates of the line positions, intensities, and line-shape parameters were incorporated into the carbon dioxide line list of the 2020 edition of the HITRAN spectroscopic database [16]. The remainder of this paper is organized as follows. In Section 2, we present an overview of CO_2 line lists in the HITRAN2016, ExoMol, Ames, and CDSD-296 spectroscopic databases. In Section 3, we describe evaluations of the HITRAN CO_2 line list based on laboratory and atmospheric measurements between 670 and 8310 cm^{-1}. For wavenumbers below 8000 cm^{-1}, we discuss line intensity updates to the HITRAN2016 line list for bands provided by the Carbon Dioxide Spectroscopic Databank (CDSD) based on global fits of semi-empirical models to measurements and those obtained by the *ab initio* calculations of University College London (UCL). In Section 4, we discuss new measurements with sub-percent relative uncertainty [19–22] that were used to improve some CO_2 bands in the 1.4 to 2.1-μm region. In Section 5, we present new CO_2 bands above 8000 cm^{-1} that have been included in the HITRAN2020 edition from the latest high-temperature line list of the ExoMol [18] database (with appropriate cut-off) for the main CO_2 isotopologue and the CRDS spectra [14] for the $^{16}O^{12}C^{18}O$ isotopologue. The line parameters of the $\nu_2+\nu_3$ magnetic dipole band of the $^{12}C^{16}O_2$ isotopologue, which have been introduced into HITRAN for the first time, will be presented in Section 6. The revision which updates the air- and self-broadened line-shape parameters of CO_2, described in Ref. [13], will be discussed in Section 7. The presentation of the final version of the HITRAN2020 CO_2 line list will be given in Section 8, followed by closing discussion and conclusions in Section 9.

2. Review of the current carbon dioxide line lists

The present section describes the status of the most currently used spectroscopic databases of carbon dioxide: HITRAN2016 [12], NASA Ames [23], and the recent ExoMol [18] and CDSD-296 [17] line lists. New laboratory and atmospheric spectra helped to expose several problems in the HITRAN2016 CO_2 line list occurring in various spectral regions (for more details, see Section 3). The CDSD-296, ExoMol, and NASA Ames line lists were used to update, extend or improve the line positions and intensities, including a number of problematic bands, in the 2020 version of the HITRAN spectroscopic database [24].

The CO_2 line list for the 12 stable isotopologues in the 2016 version of HITRAN [12] contained 559874 CO_2 transitions and covered the wavenumber range of 0.757-14075.298 cm^{-1}. The HITRAN2016 data for the $^{14}C^{16}O_2$ radioactive isotopologue in HITRAN2016 were provided as static files rather than through the relational-database structure featured in HITRAN*online* [25] . The HITRAN2016 carbon dioxide line list, below 8000 cm^{-1}, comprised CDSD line positions [26] and *ab initio* line intensities from UCL [27–29] except for the bands that were identified as "sensitive"[27], where CDSD (circa 2015) intensity values were preferred. Most of the line parameters for wavenumbers in the region above 8000 cm^{-1} were taken from the 2015 version of the CDSD-296 database [26]. An extended and improved version of the CDSD for atmospheric applications (CDSD-296) was published in 2019 [17]. This database contains a computed line list based on global modelling of the line positions and intensities using the method of effective operators [30,31]. The global model of the CO_2 absorption spectrum is a polyad model with a block diagonal structure, each polyad being characterized by the polyad number $P= 2V_1+V_2+3V_3$ (where V_i are the vibrational quantum numbers). For each CO_2 isotopologue, the effective Hamiltonians and effective dipole moment parameters were fitted to measured line positions and intensities, respectively. More than 530000 spectral lines for the 12 stable isotopologues of CO_2 covering the 345-14075 cm^{-1} spectral range were included in this database. The reference temperature is 296K, and the intensity cut-off is 10^{-30} cm/molecule. A comparison between the line positions of common lines from the HITRAN2016 and CDSD-296 [17] databases versus wavenumber in the 0-14075 cm^{-1} spectral region is presented in **Fig. 1**. This plot shows the good agreement between the line positions from HITRAN2016 (mostly based on the previous CDSD version [26]) and those from the new version of the CDSD-296 [17]. As a result, most of the line positions for the 12 CO_2 isotopologues between 345 and 14075 cm^{-1} in HITRAN2020 have been updated using the CDSD-296 [17] line positions. It should be noted that the slightly updated version of the CDSD-296 database (uploaded at ftp.iao.ru as pub/CDSD-296/cdsd-296_version_1.rar) was used. This version differs from the CDSD-296 published in Tashkun et al. [17] in the following ways: (*i*) the ΔP = 6 region of the $^{16}O^{12}C^{18}O$ isotopologue was recalculated using the new set of effective dipole moment parameters; (*ii*) a total of 226 lines with vibrational quantum number Δl_2 =4 of the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{16}O^{12}C^{18}O$ isotopologues were added. The lower-state energies and the uncertainty codes were also transferred from the CDSD-296 line list to the HITRAN2020 line list.

The recent high-temperature line list from the ExoMol database (named UCL-4000) for the main isotopologue of CO_2 ($^{12}C^{16}O_2$) was published in Yurchenko et al. [15]. This line list contains almost 2.5×10^9 transitions involving about 3.5×10^6 states. The wavenumber range of the CO_2 list is from 0 to 20000 cm^{-1} with the lower-state energies up to 16000 cm^{-1} and $J\leq202$. These results were generated using UCL's *ab initio* dipole moment surface (DMS) [32] and the semi-empirical potential energy surface (PES) Ames-2 [22] with the variational program TROVE [33]. The UCL-4000 line list was converted to HITRAN format and compared with the HITRAN2016 line list. As a result, more than 3600 spectral lines above 8000 cm^{-1} were added to the HITRAN2020 spectroscopic database [24] (see Section 5).

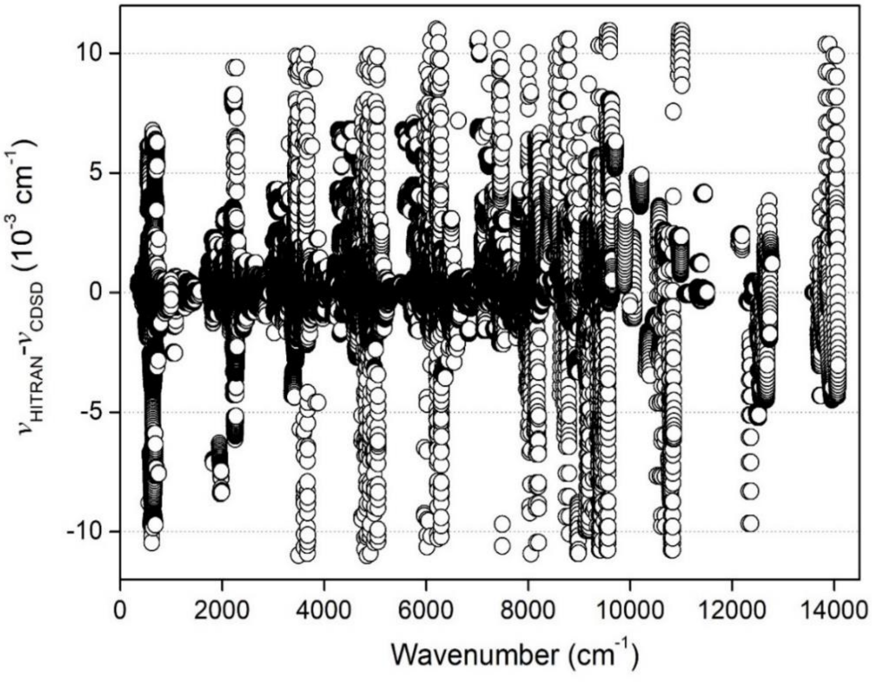


Fig. 1. Differences between the line positions from the HITRAN2016 [12] and CDSD-296 [17] databases.

The NASA Ames line lists for 13 CO_2 isotopologues were published by Huang et al. [23]. They were computed at 296 K using the empirically refined Ames-2 potential energy surface and pure *ab initio* DMS-2 dipole moment surface with *J* ≤150 and the lower-state energy up to 24000 cm^{-1}. Critical validation tests of the available spectroscopic data were carried out using the existing theoretical and semi-empirical databases, including ExoMol, NASA Ames, and CDSD-296 [17,18,23] and with published experimental works [14,34–42] .

Accordingly, the present work allowed revealing some problems with the HITRAN2016 CO_2 line list and thus allowed improving and extending the line lists for all 12 stable isotopologues in the final version of the HITRAN2020 CO_2 line list.

3. Evaluation of the HITRAN CO_2 line lists by laboratory and atmospheric spectra

In this section, we present the general review of problematic bands identified in new laboratory and atmospheric spectra, mainly those obtained from the Kitt Peak National Observatory, MkIV balloon, CRDS, and TCCON [10,14–16]. Most of the issues have been associated with deficient line positions and intensities for which critical validation tests were performed and alternative sources of data for each problematic band were suggested.

Several CO_2 line lists, including HITRAN 2008 [43], HITRAN2012 [44], and HITRAN2016 [12], were evaluated by fitting laboratory (mainly Kitt Peak) and atmospheric solar absorption spectra (MkIV and TCCON) between 670 and 8310 cm^{-1} [15,16]. The studied region was divided into several windows, most encompassing at least one complete CO_2 absorption band or a sub-branch. The GFIT spectral fitting algorithm [45] was used in all cases assuming a Voigt line profile and no line mixing. The line lists were evaluated in terms of the RMS fitting residuals and the window-to-window consistency of the retrieved gas amounts. There was no analysis of the separate isotopologues. The results showed progressive overall RMS fit improvements through use of each successive HITRAN version. This analysis showed that the HITRAN2020 CO_2 line list is substantially better than all previous HITRAN versions. In particular, in HITRAN2016, there were a few regions where it is worse than a previous version in terms of RMS fitting residuals (around 1800 cm^{-1}, 4800 cm^{-1}, and 6400 cm^{-1}). As an example, **Fig. 2** shows the absolute RMS residuals of the fits for 41 windows averaged over the 137 Kitt Peak and 12 JPL laboratory spectra in the 670-

8310 cm^{-1} spectral region. The pressure range is from 0.013 kPa-93 kPa (0.1 Torr to 700 Torr) except for 2 Kitt Peak spectra (1.71 kPa and 1.89 kPa) covering 600-1400 cm^{-1}. However, in this plot, the HITRAN2020 line list gives worse fits in the 3730 cm^{-1} window in Kitt Peak lab spectra than most previous line lists. This is due to the SBHWs being too small in this region (the Kit Peak lab spectra include some with 200 Torr of pure CO_2). This SBHW issue has no affect on fits to atmospheric spectra. The large discrepancies were also identified in the 4800 cm^{-1} regions, where the HITRAN2016 line list was worse than previous editions in terms of RMS fitting residuals. The same situation in this region was observed in the MkIV balloon spectra (low pressure). The Kitt Peak laboratory spectrum revealed rotationally-dependent errors at the 10-15% level in the *ab initio* intensities for the 40002-01101 band of the $^{12}C^{16}O_2$ isotopologue. Fits to a Kitt Peak laboratory spectrum in the 4800 cm^{-1} region and zooms into four large residuals are presented in **Fig.3**. Also, it was shown that the scatter factor of the 40002-01101 band is slightly elevated (1.4 to 1.7). In addition to that, for low *J*, around *J*=1 to 3, there is a visible spike in the scatter factor, which suggests a *J*-localized resonance. Indeed, by analyzing predictions within the effective operator model [30], it was found that the 40002 and 21113 vibrational levels of the *P*= 8 polyads are interacting through a Coriolis interaction. This interaction causes systematic problems with the *ab initio* intensities [27] for the transitions involving either of these two vibrational states.

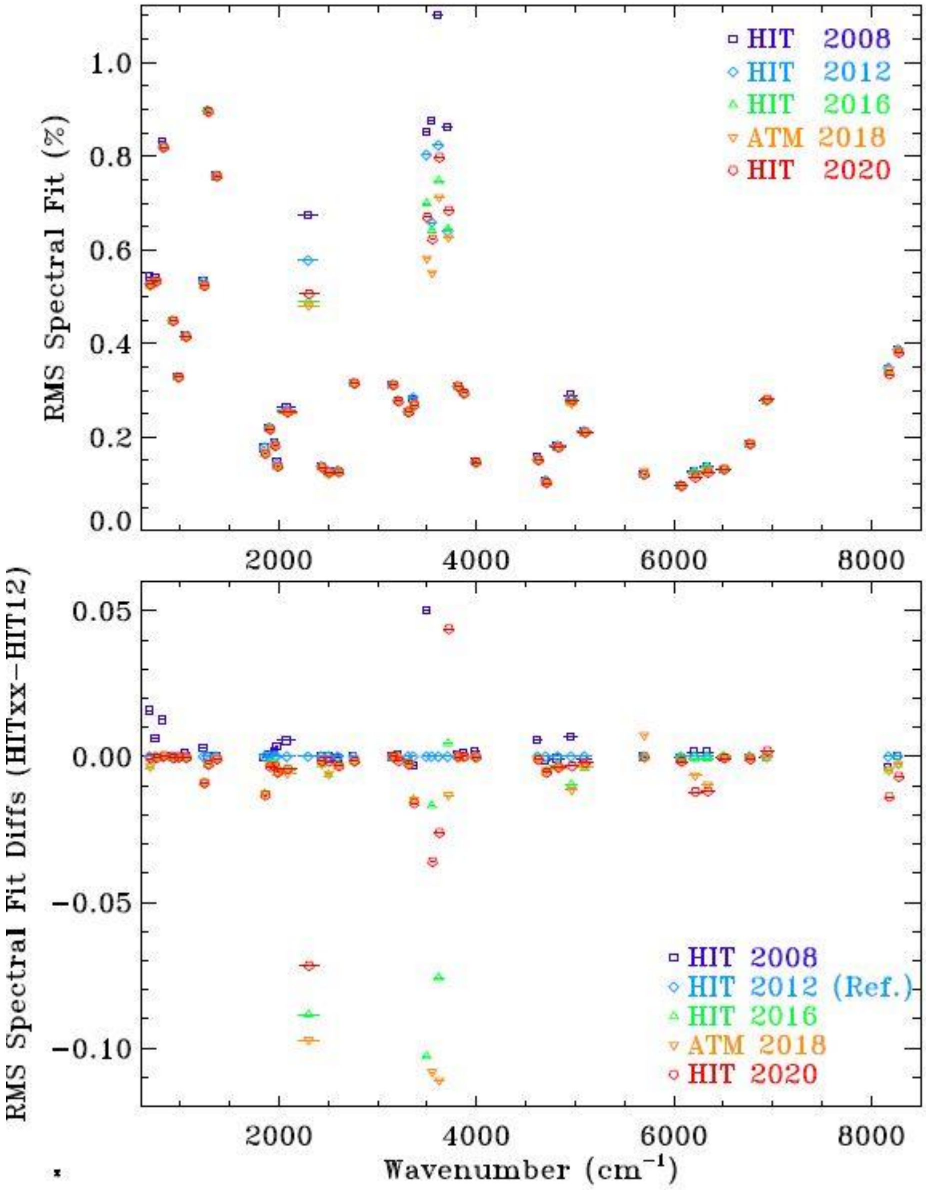


Fig. 2. The upper panel shows the absolute value of the mean *RMS* fit for 5 different CO_2 line lists: HIT2008: HITRAN2008 [43]; HIT2012: HITRAN2012 [44], HIT2016: HITRAN2016[12], ATM2018: 523230 CO_2 lines [15], HIT2020: HITRAN2020 [24]. The lower panel shows the differences from HITRAN2012 [44].

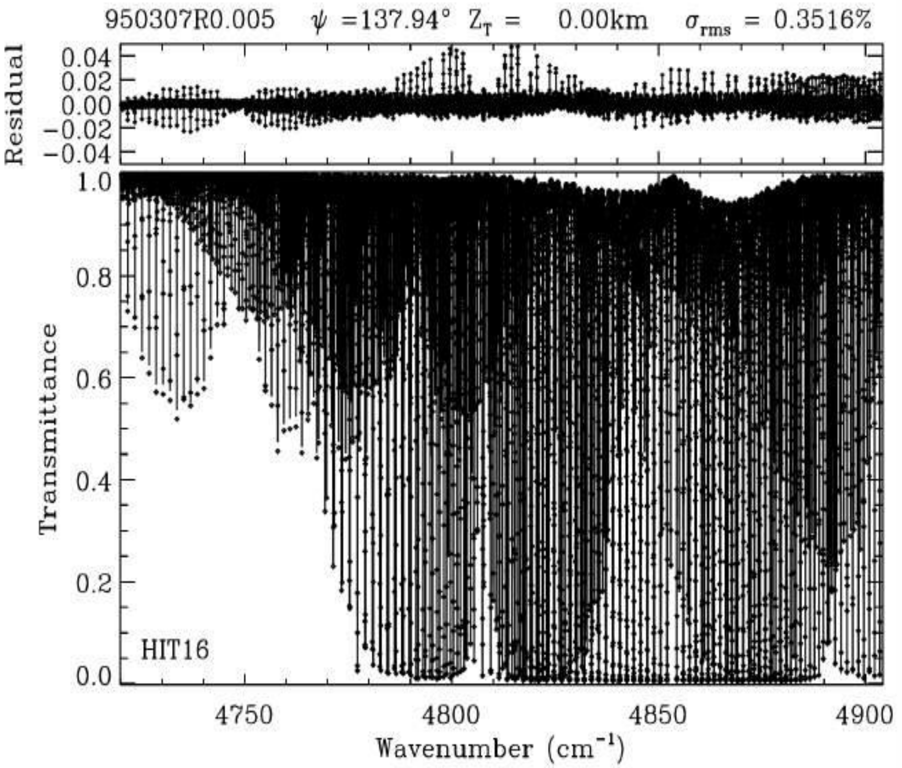


Fig.3. The fits to a Kitt Peak laboratory spectrum in the 4800 cm^{-1} region using the HITRAN2016 linelist [12]. The positive residuals arise from the 40002-01101 band of the $^{12}C^{16}O_2$ isotopologue.

For the HITRAN2016 CO_2 line list, there are 24 bands involving the 40002 and 21113 vibrational levels affected by Coriolis interaction. To quantify the impact of this perturbation on intensities, validation tests for the 40002 - 01101, 21113 - 01101, and 21113 - 11102 bands of the $^{12}C^{16}O_2$ isotopologue were carried out using the published experimental values [34,35] and data from the various carbon dioxide spectroscopic databases [12,17,23] (**Fig. 4**). This comparison showed that the CDSD-296 line intensities [17] are preferable for the 40002 - 01101 and 21113 - 11102 bands whereas, in the case of the 21113-01101 band, the *ab initio* intensities from AMES [23] are the best choice. However, because of the lack of measurements we could not make similar comparisons for the numerous remaining bands affected by these Coriolis interactions. We hope that new experimental data will become available for further validation tests of bands involving the 40002 and 21113 vibrational levels.

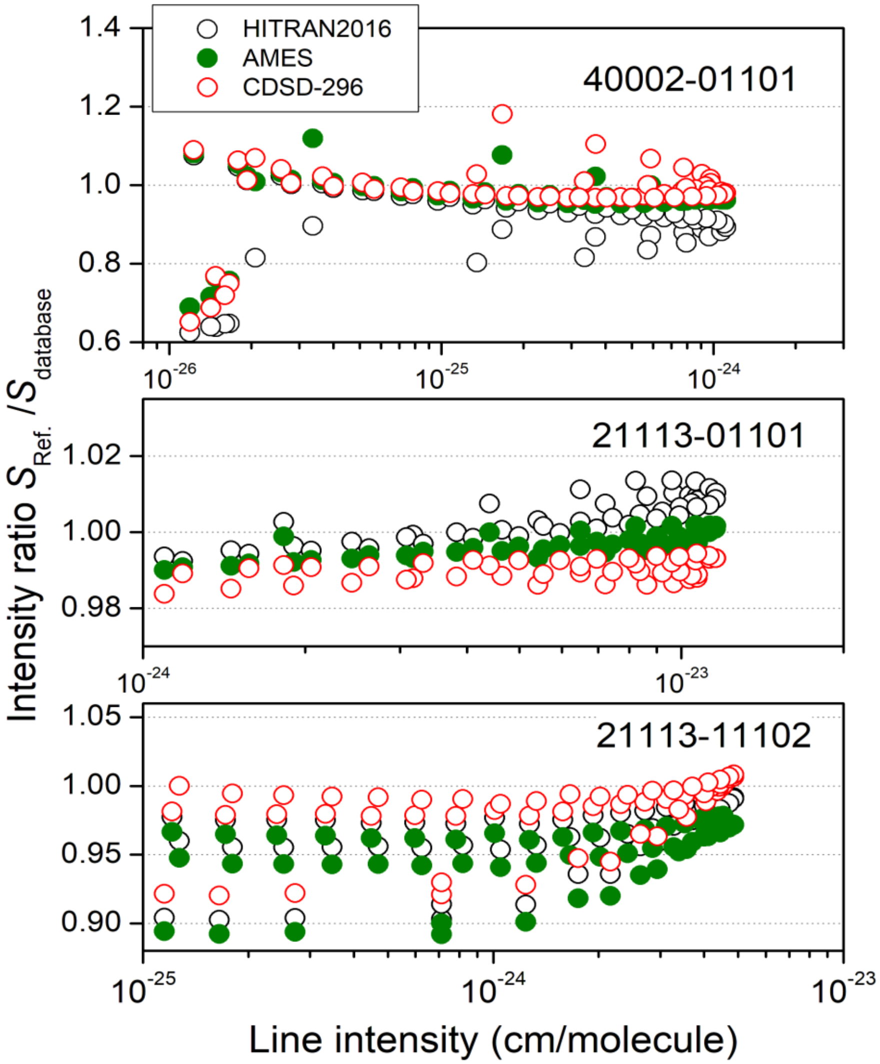


Fig.4. Ratio of the experimental line intensities of the 40002 - 01101, 21113 - 01101, and 21113 - 11102 bands (centers: 4808 cm^{-1}, 4809 cm^{-1}, and 3544 cm^{-1}, respectively) from Refs [34,35] to those from the various CO_2 spectroscopic databases [12,17,23] .

In the 1800-2000 cm^{-1} spectral region, CO_2 retrievals of mixing ratio based on the HITRAN2016 database produces CO_2 retrieved amounts that are 5% larger than those based on previous line lists. The VMR Scale Factors (VSF) obtained by averaging each retrieved single-spectrum VFS value over all 19 MkIV balloon spectra that were fitted for each window are plotted versus wavenumber in **Fig. 5**. The MkIV instrument simultaneously records the region 600 cm^{-1}

to 5650 cm^{-1}, so derived VSFs should have good window-to-window consistency. The upper circle indicates anomalously high HITRAN2016 values in the 1800-2000 cm^{-1} spectral region corroborating observation in laboratory spectra.

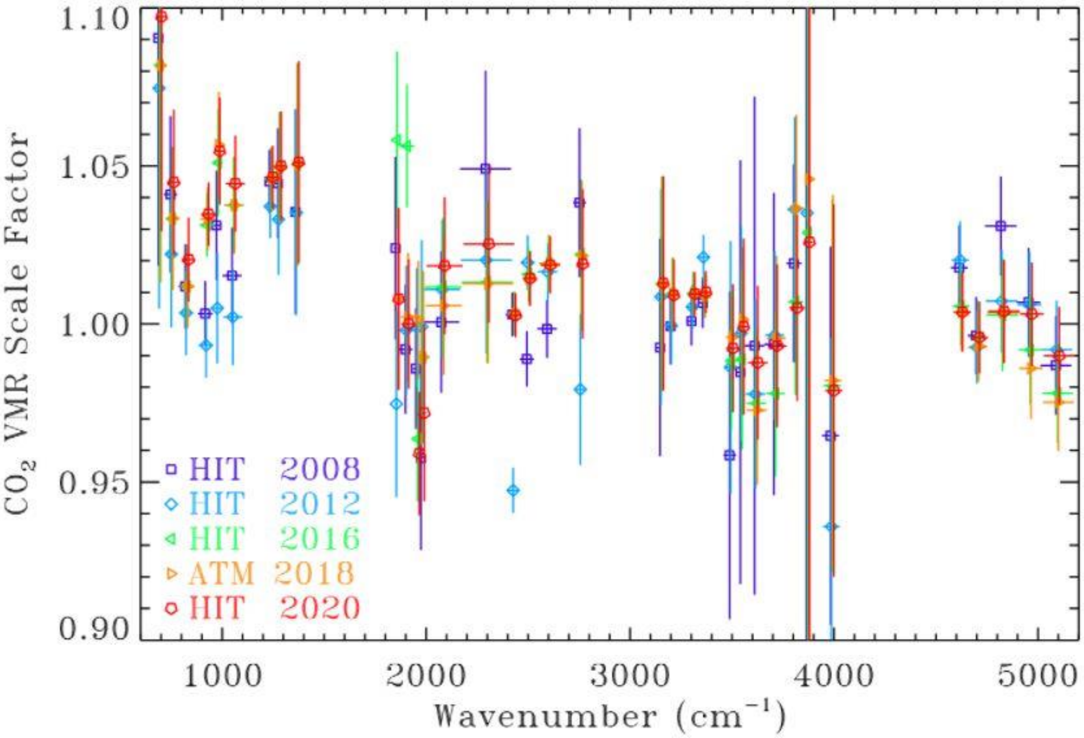


Fig.5. The VMR Scale Factors (VSF) obtained by averaging each retrieved single-spectrum VFS value over all 19 MkIV balloon spectra that were fitted for each window. The measured VSF values are plotted *versus* wavenumber. See the designations of the databases in the caption of Fig. 2.

It was found that the most significant deviations in this region correspond to the 11102 - 00001 band near 1933 cm^{-1}. The 11101 - 00001 and 11102 - 00001 bands borrow intensities from the strong 00011 - 00001 band *via* Coriolis interaction. It was shown in Ref. [17] that the *ab initio* AMES line intensities [23] for the 11101 - 00001 band deviate considerably from the observations. A comparison of the 11102 - 00001 line intensities with the published measurements [36,37] and the different CO_2 databases [12,17,23] for the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{16}O^{12}C^{18}O$ isotopologues is presented in **Fig. 6**. Replacement of line intensities of the CO_2 bands considered in the HITRAN2016 database with CDSD-296 [17] rectifies the above-mentioned discrepancy in the 1800-2000 cm^{-1} region. For consistency, the line intensities of the 11101 -

00001 band for other CO_2 isotopologues were also replaced by the intensities from the CDSD database in the HITRAN2020 line list. The 20003-01101 and 12202-01101 hot bands of $^{12}C^{16}O_2$ located near 1900 cm^{-1} were also increased by 5% to match the ATM values [15]. The intensity origin for these bands in HITRAN2016: 20003-01101 – UCL *ab initio* [27] and 12202-01101 – UCL *ab initio* and CDSD2015 [26,27]. Also, the comparison of the ATM and CDSD2019 line intensities showed a deviation up to 30% for the 20003- 01101 band of the $^{12}C^{16}O_2$ isotopologue.

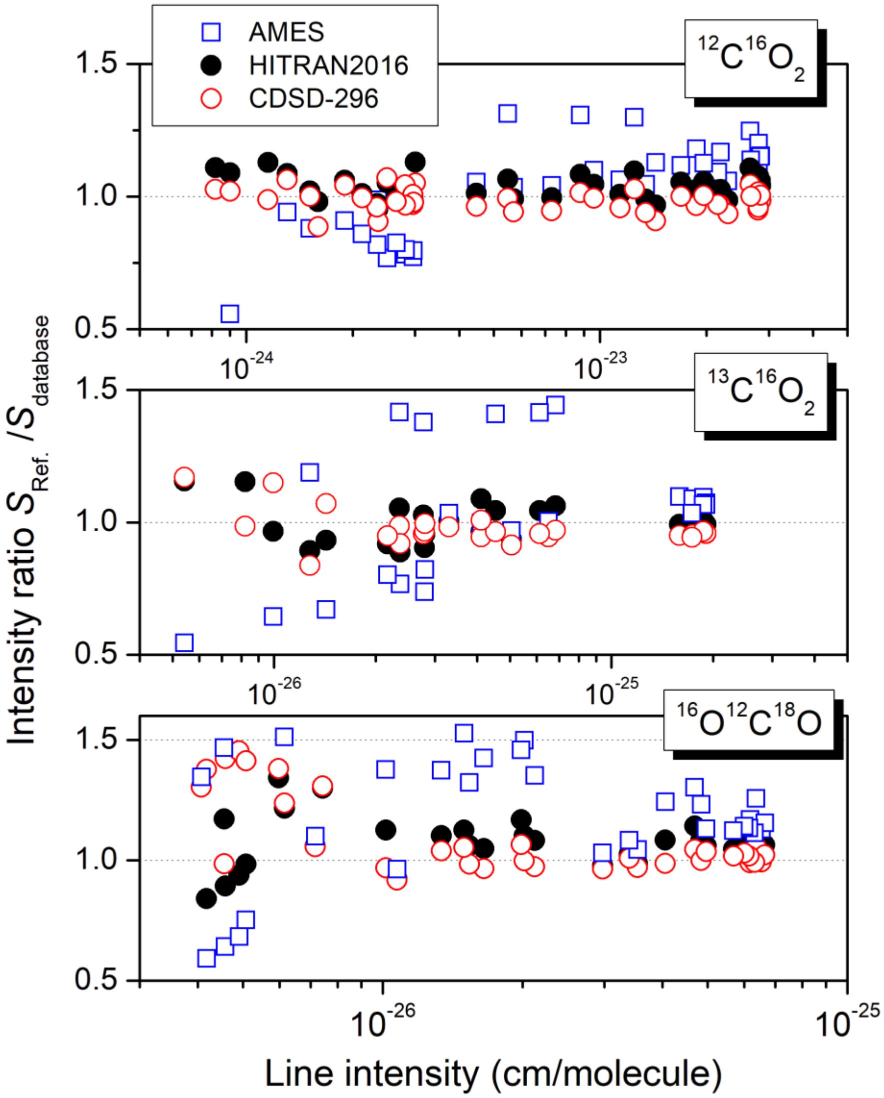


Fig. 6. The comparison of line intensities between the published measurements from Refs [36,37] and the different CO_2 databases [12,17,23] for the 11102-00001 bands of the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{16}O^{12}C^{18}O$ isotopologues with centers: 1933 cm^{-1}, 1897 cm^{-1}, and 1903 cm^{-1}, respectively.

The TCCON observations considered here cover the 3950 to 9500 cm^{-1} spectral region. These measurements are made with a Fourier transform spectrometer with an InGaAs detector and optical path difference (OPD) of 45 cm, corresponding to a resolution of 0.02 cm^{-1}. Use of the HITRAN2016 line lists reduces the CO_2 retrieved from the 6220 and 6338 cm^{-1} windows by 0.5% and 1.5% respectively, by comparison to results obtained with the other line lists, thus introducing a new inconsistency of 1.5%. TCCON CO_2 windows are circled in **Fig.7**. This issue is associated with the 30012 - 00001 and 30013 - 00001 line parameters and is discussed in detail in Section 4.

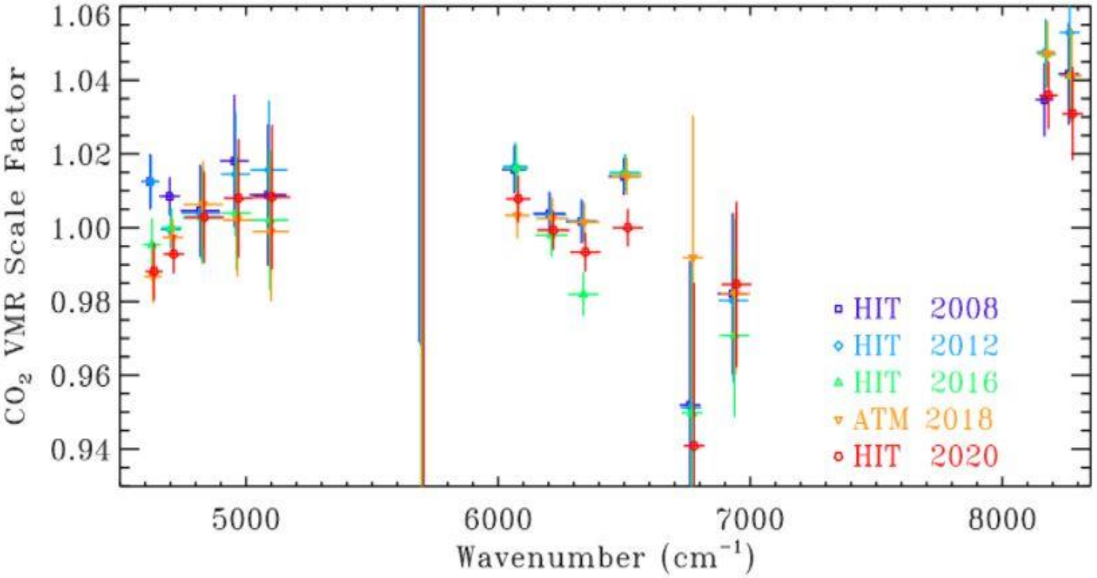


Fig.7. Retrieved VMR Scale Factors (VSF) obtained by averaging single-spectrum based on fitting each spectral window from the TCCON spectra. Results are plotted versus wavenumber. See the designations of the databases in the caption of Fig. 2.

The comparison of the fits to 136 Kitt Peak lab spectra with those modeled using the HITRAN2016 CO_2 line list shows large residuals in the 3500 and 4800 cm^{-1} spectral windows due to inaccuracies of line positions of the 10012-0001, 20012-00001, and 20013-00001 bands of the $^{13}C^{16}O_2$ isotopologue. The comparison showed that the HITRAN2012 [44] line positions for the 20012-00001 and 20013-00001 bands led to better residuals than those of the HITRAN2016 and CDSD-296 [17] databases. As a result, the line positions of the 20012 - 00001 and 20013 - 00001 bands of the $^{13}C^{16}O_2$ isotopologue were replaced with the corresponding HITRAN2012 line positions into the HITRAN2020 CO_2 line list. In the case of the 10012-00001 band, we subtracted

0.0009 cm^{-1} from the CDSD [17] line positions used for this band in HITRAN2020 to match the ATM values [15].

Also, inaccuracies in the positions of some $^{16}O^{12}C^{18}O$ lines of the 01121-01101 hot band (P13e, P14e, P14f, Q12f, Q13e, Q13f, R11e, R12e, and R12f) were evidenced in the HITRAN2016 line list between 4600 and 4625 cm^{-1}. This issue was identified by comparison with fits to Kitt Peak spectra and was solved by replacing the line positions with positions from the CDSD-296 database [17] in the HITRAN2020 CO_2 line list.

As mentioned above, below 8000 cm^{-1}, most line intensities in the HITRAN2016 database came from the UCL-IAO line lists [27–29] which are based on *ab initio* calculations. Because of excessive uncertainty in the *ab initio* line positions, the HITRAN 2016 line list is, in general, a combination of the CDSD- based line positions [26] and the UCL variational line intensities [27–29]. In the case of the so-called "sensitive bands" (as defined by Zak et al. [27–29]) *ab initio* intensities were replaced with those from CDSD when available. This substitution resulted in some cases where transitions in a given band would have intensities from both *ab initio* calculations as well as those from CDSD. Although this approach was justified in many cases, a number of inconsistencies in the rotational distribution of intensities in HITRAN2016 were revealed in CRDS spectra of ^{18}O and ^{13}C enriched and natural CO_2 near 1.74 µm [39,40,46]. In these works, the anomalies involve the perpendicular bands of the ΔP= 9 series of transitions. As shown in **Fig 8**, the mixing of CDSD and UCL *ab initio* intensities for the 41104-00001 bands of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ isotopologues leads to an apparent inconsistency in the rotational dependence with strong intensity variation between successive J values or even missing transitions. A similar situation was found in the case of the 41104-00001 band of $^{16}O^{12}C^{18}O$ isotopologue (See **Fig. 9**). A comparison of the measurements from Refs [39,40,46] to various carbon dioxide spectroscopic databases is presented in **Fig. 10**. As can be seen from this figure, the AMES intensity values for this band are all close to the experimental ones. As a result, for HITRAN2020, the AMES intensities of the 41104-00001 bands of the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{16}O^{12}C^{18}O$ isotopologues were preferred to the mixed intensity values in the HITRAN2016 line list.

Similar validation tests using the values available in the literature and from the different CO_2 databases were carried out for other bands affected by the problem due to the mixing of intensities of CDSD and *ab initio* origin in the HITRAN line list. These bands were systematically searched (see Fig. 5 of Ref.[39]), and when problems were identified, alternative sources of data for each such bands were suggested. For the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{16}O^{12}C^{18}O$, and $^{16}O^{13}C^{18}O$ isotopologues, we present in Table 1 the set of bands that were checked and affected by this issue along with the alternative intensity sources for these bands used in HITRAN2020. The substitution of the suggested intensity sources for the bands presented in Table 1 was performed for the corresponding bands of all the CO_2 isotopologues in HITRAN2020 where experimental data exists. In the absence of experimental reference data, the replacement of the intensity source was performed only for the corresponding band of the specific isotopologue. In the case of the 31104e-01101e and 11112e-11101e hot bands of the $^{16}O^{12}C^{18}O$ and $^{13}C^{16}O_2$ isotopologues, respectively (see **Fig.11**), we cannot offer an alternative source for replacing the mixed line intensities, since there is no experimental data to verify them. Nevertheless, we kept the HITRAN2016 line intensities for the 31114e-01101e band of $^{16}O^{12}C^{18}O$ isotopologue in HITRAN2020. In the future we will consider using UCL *ab initio* [28] line intensities for this band. In the case of the 11112e-11101e hot band of the $^{13}C^{16}O_2$ isotopologue, the UCL and CDSD-296 databases [17,27] give similar line intensities although there is an inconsistency in the rotational dependence with substantial intensity variation between successive *J* values of the *P* branch. Validation of this band is a challenge for future experiments.

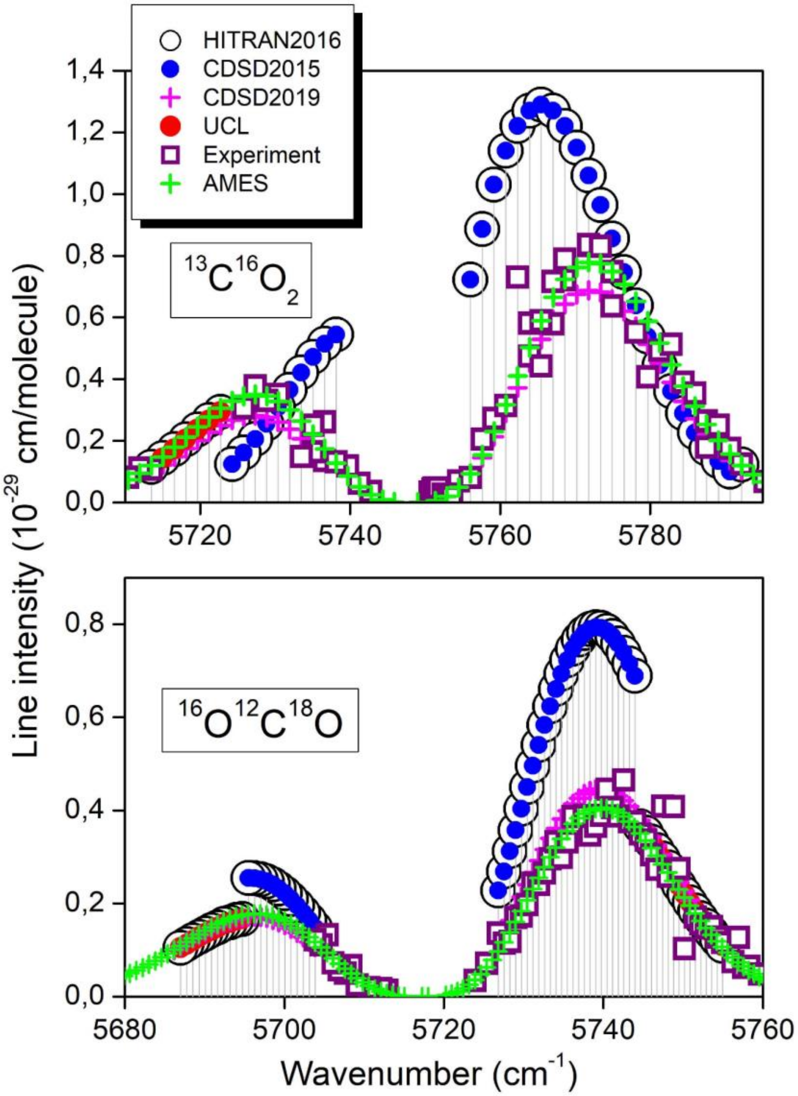


Fig. 8. Comparison of the CRDS measurements (purple squares) of the 41104 - 00001 band of $^{13}C^{16}O_2$ [46] and $^{16}O^{12}C^{18}O$ [40] to various databases: HITRAN2016 [44], CDSD-296 (CDSD2015) [26], CDSD-296 (CDSD2019) [17], UCL [27,28], and AMES [23] line lists.

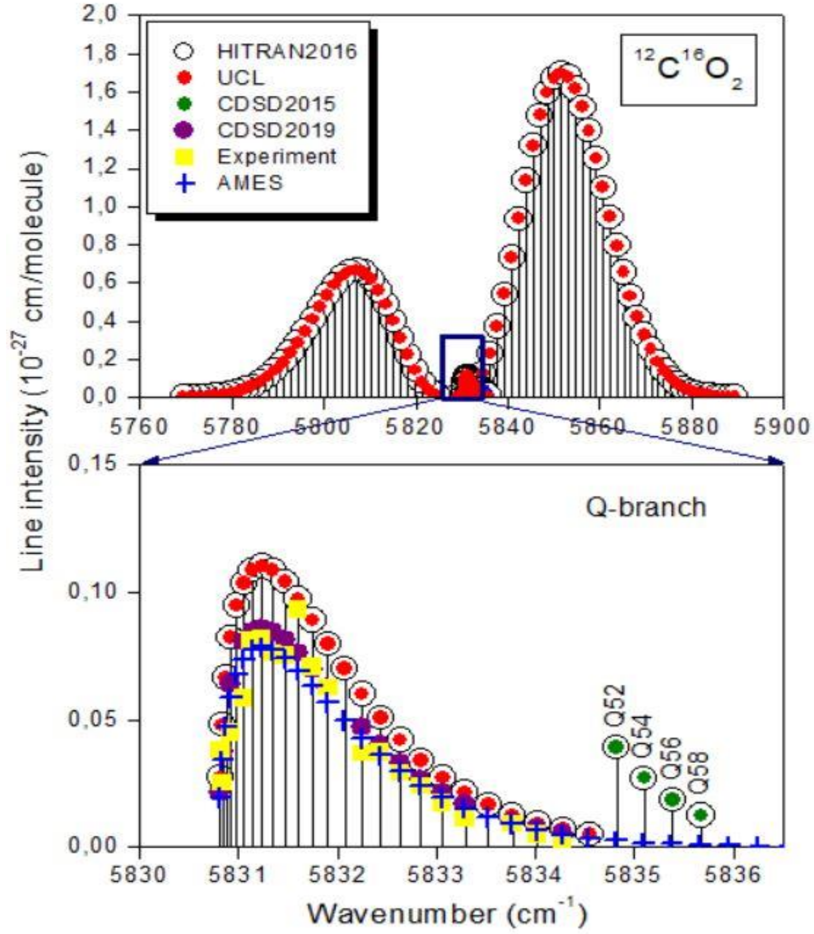


Fig.9. Overview comparison of the *Q*-branch of the 41104 - 00001 band of $^{12}C^{16}O_2$ [39] to the HITRAN2016[12], CDSD-296 (CDSD2015) [26], CDSD-296 (CDSD2019) [17], UCL [27] and AMES [23] line lists. The lower panel highlights the *Q* branch where the HITRAN2016 list uses UCL and CDSD2015 as intensity sources for *J* below 50 and above 52, respectively, leading to the observed intensity jump between *Q*(50) and *Q*(52). The CRDS measurements [39] validate the AMES intensity values which were taken as the unique source for HITRAN2020 of this band.

Table 1. The bands for the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{16}O^{12}C^{18}O$, and $^{16}O^{13}C^{18}O$ isotopologues where intensities were from mixed sources in HITRAN2016 and the new sources of intensities chosen for HITRAN2020.

Band	Band center (cm^{-1})	Intensity origin		Experimental works
		HITRAN2016	HITRAN2020	
$^{12}C^{16}O_2$ isotopologue				
21103-02201	1846.33	[26,27]	[26,27]	-
13302-02201	1907.85	[26,27]	[27]	-
20002-01101	2003.76	[26,27]	[17]	[41]
21102-10002	2054.72	[26,27]	[27,28]	-
22201-11101	2120.50	[26,27]	[17]	[42]
40002-21103	2295.65	[26,27]	[27]	-
30004-01101	3125.10	[26,27]	[17]	[34]
31104-10002	3131.52	[26,27]	[27]	-
22203-01101	3156.20	[26,27]	[27]	-
31103-10002	3306.48	[26,27]	[27]	-
22202-01101	3342.10	[26,27]	[27]	-
23302-02201	3344.01	[26,27]	[27]	-
31102-10001	3365.31	[26,27]	[17]	[34]
30002-01101	3398.45	[26,27]	[27]	-
21101-00001	3501.45	[26,27]	[27]	-
40002-11102	3544.64	[26,27]	[27]	-
01121-10002	4031.07	[26,27]	[27]	-
31104-00001	4416.15	[26,27]	[17]	[35]
41103-10001	4613.12	[26,27]	[27]	-
25501-02201	4696.61	[26,27]	[27]	-
10021-01101	5346.31	[26,27]	[17]	[47]
50006-01101	5572.65	[26,27]	[27]	-
50005-01101	5768.12	[26,27]	[27]	[39]
42204-01101	5805.64	[26,27]	[17]	[39]
41104-00001	5830.79	[26,27]	[23]	[39]
50004-01101	5920.94	[26,27]	[27]	-
50003-01101	6057.89	[26,27]	[27]	[48]

$^{13}C^{16}O_2$ isotopologue				
04421-01101	1946.12	[26,29]	[27,28]	-
11112-11101	2110.13	[26,27]	[27]	-
$^{16}O^{12}C^{18}O$ isotopologue				
31104-30004	616.12	[26,28]	[17,28]	-
21101-10002	2195.21	[27,28]	[28]	-
21101-00001	3454.63	[27,28]	[28]	-
31104-01101	3677.44	[26,28]	[28]	-
$^{16}O^{13}C^{18}O$ isotopologue				
12202-01101	1856.75	[26,28]	[28]	-

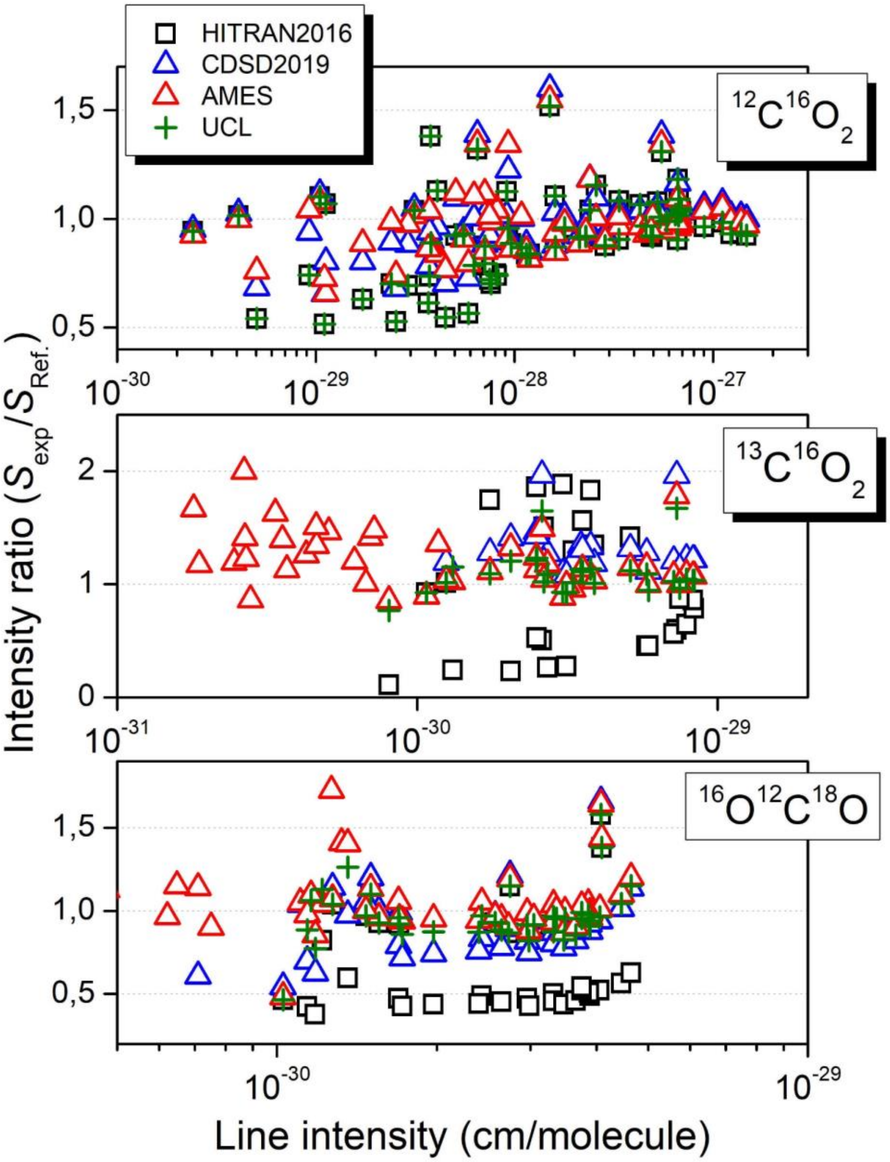


Fig.10. Ratios of the measured line intensities of the 41104 - 00001 band of the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{16}O^{12}C^{18}O$ [39,40,46] isotopologues to the HITRAN2016 [12], CDSD-296 (CDSD2019) [17], UCL [27,28] and AMES [23] line lists.

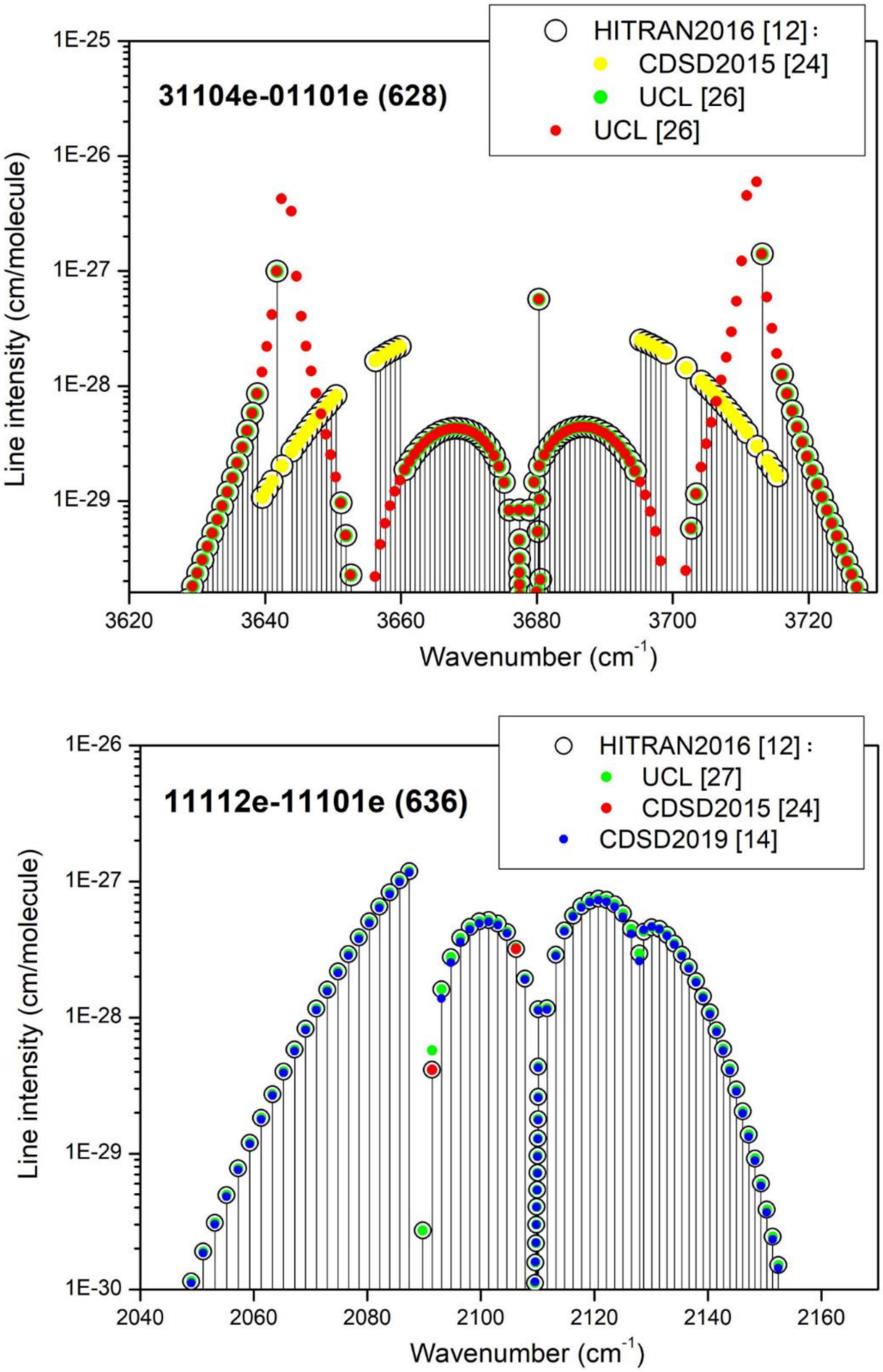


Fig. 11. The 31104e-01101e and 11112e-11101e hot bands of $^{16}O^{12}C^{18}O$ (628) and $^{13}C^{16}O_2$ (636) isotopologues, respectively, having the mixed line intensities in the HITRAN2016 database [12].

4. New experimental data with sub-percent uncertainty

Accurate line parameters of the spectral lines are generally required for the most demanding atmospheric applications. In particular, the accurate values of the line intensities with uncertainties as low as 0.3%-0.5% [49] are necessary for forward models used in retrievals of CO_2 concentrations from some remote sensing missions. A number of very accurate measurements have become available after the release of HITRAN2016 in the NIR region: the most recent CRDS measurements from NIST [19,20] and FTS measurements from DLR reported in Birk et al. [22] (with the corresponding measurements and line parameter database provided on Zenodo [21]). The results obtained in these works were used to improve the HITRAN line intensities of the $^{12}C^{16}O_2$ isotopologue.

The accurate CRDS line intensity measurements for the 3001*i*–00001 (*i* = 2-4) bands reported by Long et al. [19] were used to refine the calculated HITRAN2016 CO_2 band intensities near 1.6 µm. This region is actively used for spectroscopic measurements of atmospheric CO_2 concentrations. For instance, the 30013–00001 band is targeted by the OCO-2 and OCO-3 missions [5,7], while the 30012–00001 band is used for the LIDAR missions [50]. It was shown in Ref. [19] that the band-integrated CRDS intensity measurements and the *ab initio* calculations of Zak et al. [27] agree at the 0.06% level for the 30013–00001 and 30014–00001 bands, but there is a systematic discrepancy of about 1.1% for the 30012–00001 band. We note that the HITRAN2016 line intensities are from the *ab initio* UCL results [27], and they have relative uncertainties < 2 % for the 30012 - 00001 and 30013 - 00001 bands and < 5 % for the 30014 - 00001 band, respectively. In contrast, the current CO_2 spectroscopic databases [17,23] show a significant spread in their line intensities at about or above 1%. Following these results [19], the HITRAN2016 line intensities for the 3001*i*–00001 (*i*=2-4) bands were scaled to the recommended band-dependent scaling constant factors, while preserving the original *J*-dependence of the ab initio calculations. The comparison of the HITRAN2016 and HITRAN2020 line intensities of the 30012-00001 band of $^{12}C^{16}O_2$ isotopologue to the experimental values reported in Long et al. [19] is plotted in **Fig.12**.

In Fleurbaey et al. [20], it was shown that a constant scaling of 1.0069±0.0002 of HITRAN2016 values in the 20013–00001 band of CO_2 near 2.06 µm is consistent with the experiment. Therefore, we have performed this scaling in HITRAN2020. In Refs [19,20], the reported relative uncertainty in intensity is better than 0.1%, thus the uncertainty code 8 (< 1%) for the line intensities was given for the corresponding bands in the HITRAN2020 line list.

Bruker IFS 125HR Fourier-transform spectrometer measurements have been conducted at the German Aerospace Center (DLR) to measure pure carbon dioxide transmittance spectra in the 6000–7000 cm^{-1} spectral region, including the 30011 - 00001, 30012 - 00001, 30013 - 00001, 30014 - 00001, and 00031 - 00001 bands [22] . In this work, line intensity uncertainties of 0.15% were reported. The scaling factor 1.0061 was used for the HITRAN2016 line intensities of the 30011 - 00001 band of the $^{12}C^{16}O_2$ isotopologue to match with DLR measurements [22]. The 30013 - 00001 and 30014 - 00001 HITRAN2016 line intensities and NIST measurements were found to be in good agreement with the DLR measurements. However, for the 30012 - 00001 band, the differences outside of the stated uncertainties with both NIST measurements and HITRAN2016 were reported. The difference for the 30012-00001 band was 1.6%, whereas for Long et al. [19] the difference was about 1%. It should be noted that these differences are outside the stated uncertainty budget. In addition, the DLR data showed systematic differences of relative line intensities to HITRAN2016 within the 3001*i*-00001 (*i*=2,3) bands on the order of 0.3%.

In the HITRAN2016 edition, the line intensities of the 00031–00001 band of the $^{12}C^{16}O_2$ isotopologue near 1.4 µm used CDSD-296 [26] as an intensity source because this band was identified as "sensitive" in the *ab initio* calculations [27]. The comparison of the CDSD line intensities with the DLR measurements [20] showed rotationally-dependent deviations up to 4%. To improve the 00031–00001 line intensities in the HITRAN2020 line list, we scaled the UCL line intensities [27] by the factor of 1.1217 to match the line intensities reported by Birk et al. [22] (See **Fig. 12**). It should be noted that two lines (P20 and R18) were absent in the UCL line list [27], so that the intensities of these corresponding lines were updated from Birk et al. [22].

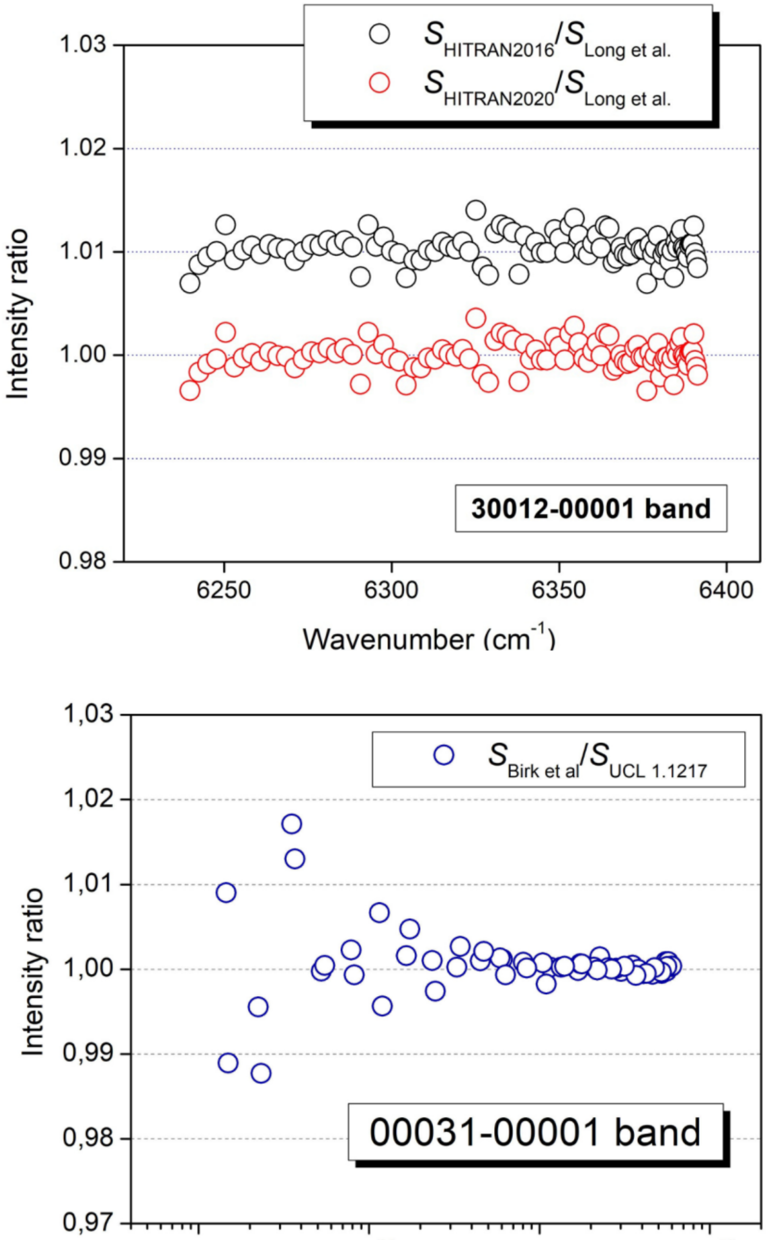


Fig. 12. *Upper panel:* Comparison of the HITRAN2016 and HITRAN2020 line intensities of the 30012-00001 band of $^{12}C^{16}O_2$ isotopologue to the experimental values measured by Long et al. [19]. *Lower panel:* Comparison of the measured line intensities reported in Birk et al. [22] and the UCL intensities scaled by the factor of 1.1217 for the 00031-00001 band of the $^{12}C^{16}O_2$ isotopologue.

The weak 10032 - 10002 and 01131 - 01101 hot bands of the $^{12}C^{16}O_2$ isotopologue located near 6900 cm^{-1} were also compared to the DLR measurements [22]. It was found that the HITRAN2016 line intensities of the 10032 - 10002 band should be scaled by a factor of 1.1346 while the line intensities of the 01131 - 01101 band having the intensity origin from CDSD-296K [26] should be scaled by a factor of 1.0022.

5. New bands above 8000 cm^{-1}

The recent high-temperature ExoMol UCL-4000 line list containing almost 2.5×10^{9} transitions at T=4000K for the $^{12}C^{16}O_2$ isotopologue was published in Ref. [18]. To compare this line list with HITRAN2016, we converted UCL-4000 to HITRAN format at 296 K and applied an intensity cut-off of 10^{-30} cm/molecule using the ExoMol_to_HITRAN.py program downloaded from http://exomol.com/software/[51]. This code transfers the position, intensity, Einstein A, lower state energy, and upper/lower level statistical weights into the correct location for a HITRAN default format ".par" file. It works by looking at the "trans" file to get the upper and lower state ID. We edited this program to extract the m_1, m_2, l_2, m_3 HITRAN quantum numbers from the ExoMol files. In the case where the states were not assigned, the vibrational assignments were replaced with "-2-2-2-20". When it was possible, we also performed additional assignments using the CDSD-296 [17] and Ames [23] databases. **Fig. 13** gives an overview comparison of the HITRAN 2016 line list to the UCL-4000 line list for the $^{12}C^{16}O_2$ isotopologue from 0 to 20000 cm^{-1}. It should be noted that the $^{12}C^{16}O_2$ line list in HITRAN2016 was limited to the spectral range 158.302 to 14075.298 cm ^{1}. In **Fig.13**, only the new bands from the UCL-4000 line list, which are missing in the HITRAN spectroscopic database, are presented. They are highlighted in blue. Most of these bands are located above 8000 cm^{-1}. Over 3600 spectral lines with line intensities from 1.8×10^{-28} to 9.9×10^{-30} cm/molecule from the UCL-4000 line list were included in the HITRAN2020 spectroscopic database. The line positions in the UCL-4000 dataset [18] are calculated from the energy levels derived from the HITRAN2016 database. Due to diversity of data in HITRAN some inconsistencies could occur when deriving upper state energy levels, which could result in the deviations. It is important to point out that the UCL-4000 line list has an issue regarding the matching of line positions. As an example, this case is shown in **Fig.**

14, where the comparison of the line positions for the 50015 - 00001 and 60014 - 10002 bands of the $^{12}C^{16}O_2$ isotopologue is presented. We traced the source of the discrepancies in UCL-4000 to the procedure used to substitute the variational (upper) state energies with the empirical values. The substituted energies were taken from HITRAN2016, either as the lower state energy term values E" or as E'= E"+*v* (where *v* is the transition wavenumber). The examples of these upper state energies, including those shown in **Fig. 14**, were affected by inconsistency of the original line positions from different sources. Most of such inconsistency cases identified in the present analysis have been improved in HITRAN2020 and will be propagated to UCL-4000 after the release of HITRAN 2020. In case of the small number of states (~20) that are still affected by small inconsistencies in HITRAN 2020's upper states, all for the transitions well above the 8000 cm^{-1}, the CDSD synthetic data [17] will be used.

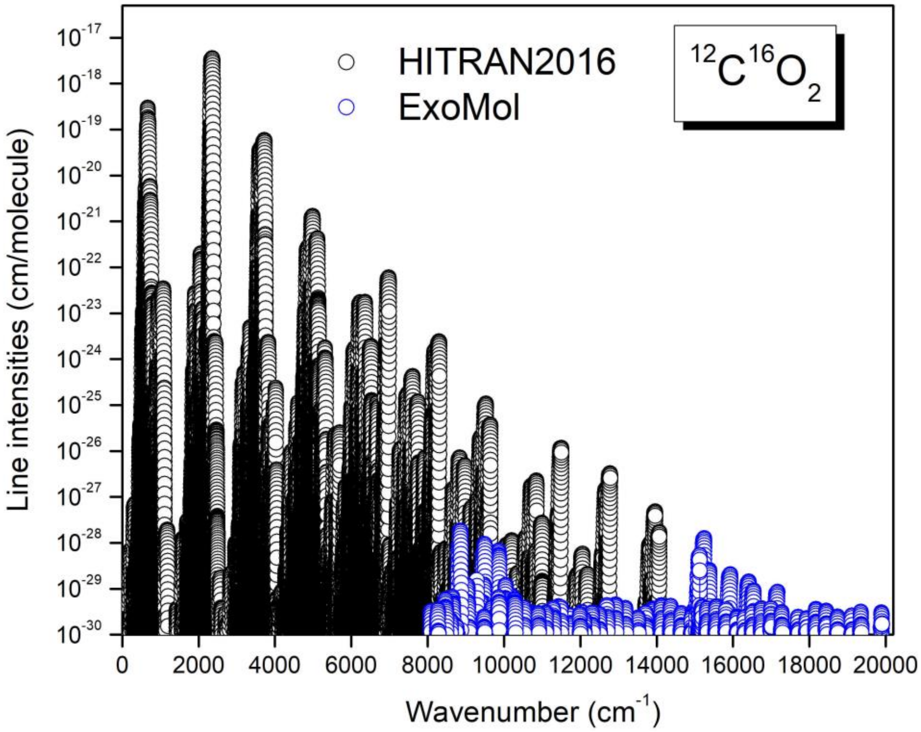


Fig. 13. Overview comparison of the HITRAN2016 [12] and ExoMol UCL-4000 [18] carbon dioxide line lists in the 0-20000 cm^{-1} spectral region.

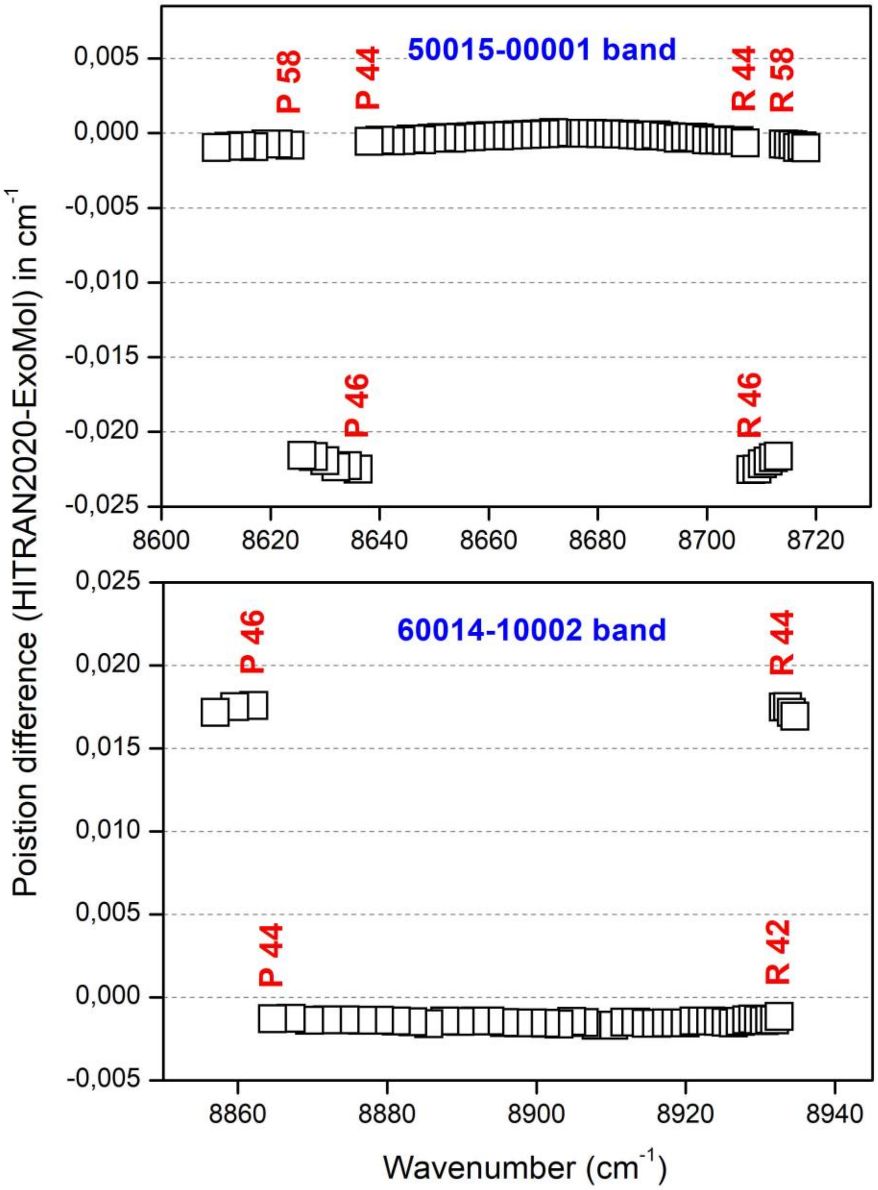


Fig. 14. Difference between the HITRAN2020 and UCL-4000 ExoMol line positions for the 50015 - 00001 and 60014 - 10002 bands of the main CO_2 isotopologue.

The weak 30022 - 00001 and 30023 - 00001 bands of the $^{16}O^{12}C^{18}O$ isotopologue with band centres as 8374.23 cm^{-1} and 8497.45 cm^{-1}, respectively, were missing in the HITRAN2016 [12] and CDSD-296 [17] spectroscopic databases. These bands were assigned in the analysis of CRDS spectra of natural CO_2 near 1.18 µm [14] and included in the new CO_2 line list. We also calculated the energy levels (thereby obtaining line positions) for the 30022 - 00001 and 30023 - 00001 bands of $^{16}O^{12}C^{18}O$ up to J_{max}=34 using the spectroscopic constants of the lower and upper state obtained in Refs [14,52] and equation (1).

$$F_v(J) = G_v + B_v J(J+1) - D_v J^2 (J+1)^2 + H_v J^3 (J+1)^3 \tag{1}$$

where G_v is the vibrational term value, B_v is the rotational constant, D_v and H_v are the centrifugal distortion constants, J is the angular momentum quantum number.

Also, it was shown in Ref. [14] that the R-branch intensities of the very weak 00041 - 01101 hot band of the $^{12}C^{16}O_2$ isotopologue, which are missing in CDSD-296 [17], are in good agreement with the NASA Ames intensities [23] while HITRAN2016 values were largely overestimated. For the HITRAN2020 database, the line intensities of the 30022-00001, 30023-00001, and 00041-01101 bands were updated using the line intensities from NASA Ames [23]. **Fig.15** shows the good agreement between the CRDS line intensities from Ref. [14] and the calculated values from the AMES line list [23]. The uncertainty codes for line positions and intensities were updated to 4 for these bands in the HITRAN2020 line list, corresponding to (≥ 0.0001 cm^{-1} and < 0.001 cm^{-1}) and (≥ 10 % and < 20 %), respectively.

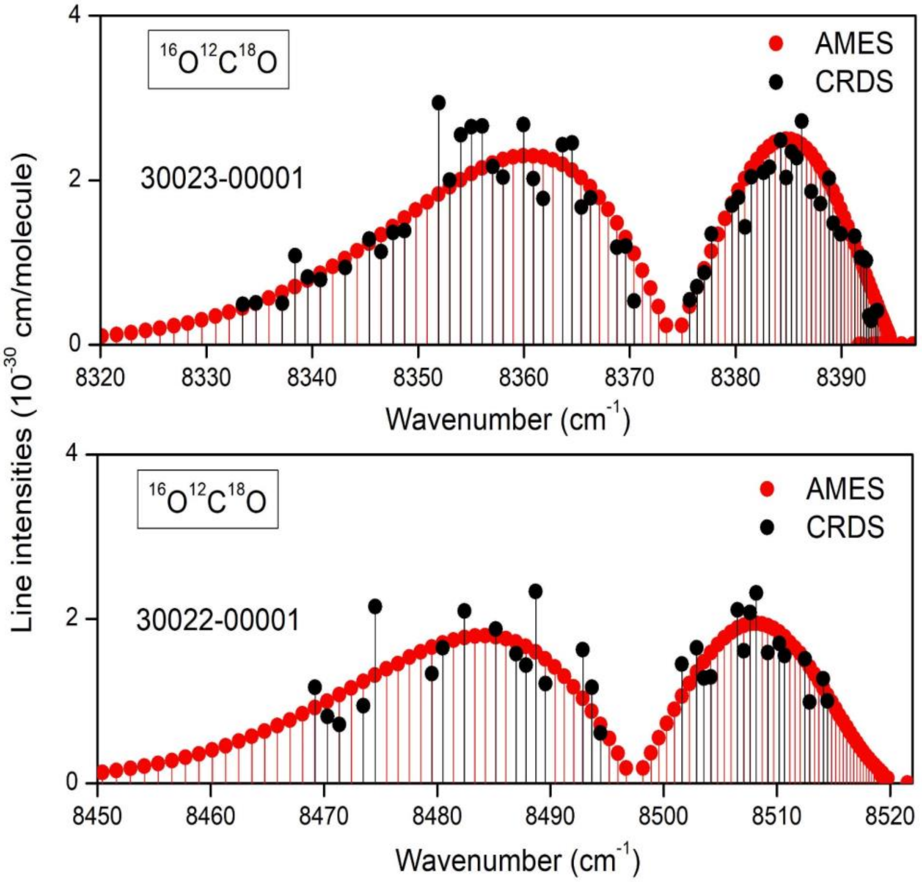


Fig.15. Comparison CRDS [14] and AMES [23] line intensities of the 30022 - 00001 and 30023 - 00001 bands of the $^{16}O^{12}C^{18}O$ isotopologue.

6. Addition of magnetic dipole band of $^{12}C^{16}O_2$ at 3.3 µm

The HITRAN2020 database has been extended by including the 01111 - 00001 (ν_2+ν_3) magnetic dipole band of the principal isotopologue of carbon dioxide. These line parameters were introduced into HITRAN for the first time; all previous editions of HITRAN provided only CO_2 electric dipole transitions. Interestingly, the first observation of the ν_2+ν_3 band has been reported at 3.3 µm in the atmosphere of Mars [53] by the ExoMars Trace Gas Orbiter ACS instrument [54]. This band is forbidden as an electric dipole absorption. However, it is allowed through electric quadrupole and the magnetic dipole mechanisms, which are typically much weaker than those allowed through the electric dipole mechanism. The maximum line intensities in the 01111-00001 band are on the order of 6×10^{-28} cm/molecule. The detailed studies of this band providing the selection rules for the vibration-rotation transitions are presented in Refs [53,55]. The vibrational transition magnetic dipole moment of the 01111-00001 band was fitted to the line intensities measured with a Bruker IFS 125 HR FTS and a 30 m base multipass gas cell of the V.E.Zuev Institute of Atmospheric Optics SB RAS [56]. The line positions and intensities of this band were computed using the vibrational transition magnetic dipole moment and the set of the effective Hamiltonian parameters reported by Majcherova et al. [57]. We included the calculated line parameters up to *J*=64 of the 01111-00001 band of $^{12}C^{16}O_2$ in the HITRAN2020 line list. The calculated line intensities were consistent with an intensity cut-off 10^{-30} cm/molecule at 296K. The calculated line intensities agree well with the values measured independently by Optical-Feedback-Cavity Enhanced Absorption Spectroscopy (OFCEAS) in Fleurbaey et al. [58] for five R-branch lines of this band (R26-R32 and R36). An overview of the 01111-00001 magnetic dipole band of the main CO_2 isotopologue with band center 3004.012 cm^{-1} is displayed in **Fig. 16**. The corresponding uncertainty codes for the line positions and intensities were used for the 01111-00001 band of $^{12}C^{16}O_2$: code 4 (≥ 0.0001 and < 0.001) and code 4 (≥ 10 % and < 20 %), respectively. It should be noted, that to distinguish the magnetic dipole transitions in the traditional HITRAN ".par" format, the letter "m" was introduced into the quantum field dedicated to upper state rotational ("local") quanta (see HITRAN2004 paper [59]).

We should also mention that in their OFCEAS study of the $\nu_2+\nu_3$ band, Fleurbaey et al. [58] reported together with the detection of the magnetic dipole lines, the measurement of weaker electric quadrupole of the same $\nu_2+\nu_3$ band. This detection was made possible by accurate *ab initio* predictions of the E2 line intensities $^{12}C^{16}O_2$ in the 0-10000 cm^{-1} range [60]. Overall, the *ab initio* intensities of the very weak quadrupole lines are validated by this OFCEAS values (maximum line intensities on the order of 10^{-28} cm/molecule). There is also evidence for these quadrupole lines in the ACS Mars spectrum [60]. The weak electric quadrupole lines are not included in the present version of the HITRAN database and will be considered for forthcoming editions.

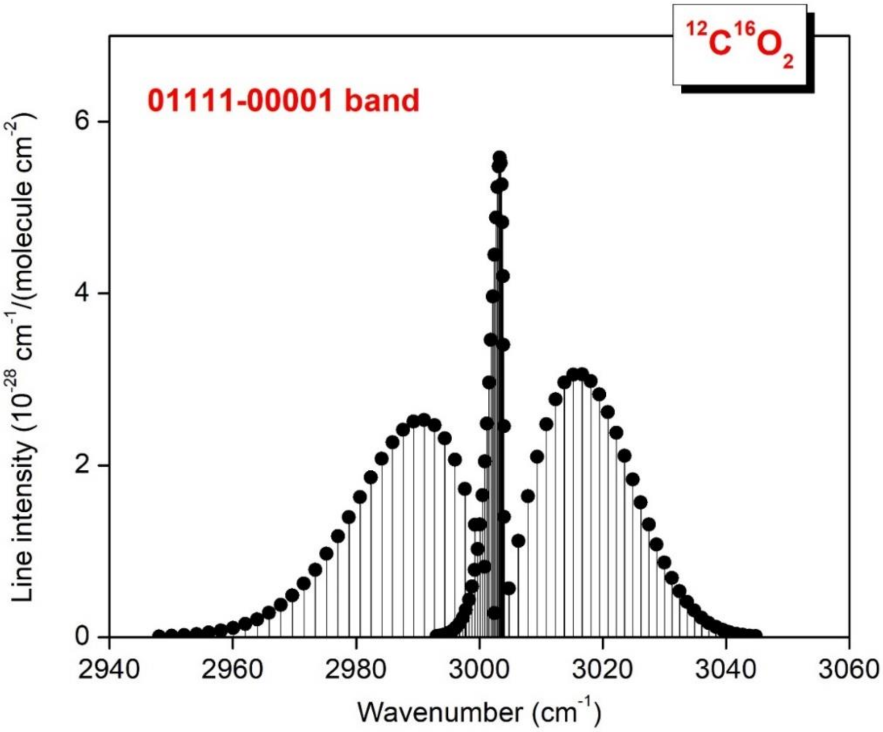


Fig. 16. The 01111-00001 magnetic dipole band of the main CO_2 isotopologue [56,58]. The band center of this band is 3004.012 cm^{-1}.

7. The line-shape parameters for the HITRAN2020 CO_2 line list

A major update of the line-shape parameters of CO_2 broadened by air and CO_2 is described in Ref. [13]; this involved both enhancing the HITRAN database and improving completeness. A systematic extrapolation method was introduced for producing the air- and self- half width (broadening) Voigt profile parameters for unmeasured transitions [61], based on the measurements reported in Ref. [62] The temperature-dependent exponents of the air- and self-broadening parameters were generated based on existing measurements and a semi-empirical calculation method using the measurements given in Refs [63,64]. Air- and self-pressure shifts for every line of CO_2 were calculated using the semi-empirical approach proposed by Hartmann [65] and fits using carefully selected experimental data.

Besides providing the standard 160-character ".par" parameter, the HITRAN2020 database will include additional parameters for the speed-dependent Voigt (SDV) profile [66,67] in a separate set. The list of the SDV parameters was provided in Table 1 of Ref. [13]. The air- and self-speed dependence of the broadening parameters with their temperature dependence will be added for all the lines of CO_2, and they can be downloaded using customized output format on www.hitran.org. One can also retrieve these parameters with the HITRAN Application Programming Interface (HAPI) [68] using the SDVoigt parameters group.

The CO_2 line-mixing package, developed by Lamouroux et al. [69] and available at HITRAN*online*, was updated using the new spectroscopic parameters obtained in the present study and the parameters found in Ref. [13].The full and the first-order line-mixing parameters have been calculated with the latter being and the first-order line-mixing parameters will be provided for every line of CO_2 in HITRAN. The new data were verified using different sets of laboratory spectra to compare with the absorption coefficient calculated by the line-mixing package program. The uncertainties better than 0.5% were achieved for the regions examined compared to HITRAN2016 (we refer to figures 16-19 in Ref. [13]), which should be beneficial for CO_2 retrieval missions, including OCO-2, ACE, and GOSAT.

8. Overview summary of the HITRAN2020 CO_2 line list

The HITRAN2020 line list for the twelve stable isotopic species of carbon dioxide contains 545084 transitions. It covers the spectral range from 0.757 cm^{-1} to 19908.186 cm^{-1} with $J \leq 128$ and with the lower-state energies up to 6533.030 cm^{-1}. Most of the line positions were replaced with line positions from CDSD-296 [17]. For the problematic line intensities identified in new laboratory and atmospheric spectra, critical validation tests were performed to improve their accuracy of the CO_2 lists. The line-shape parameters of CO_2 broadened by air and CO_2 were updated. A summary of the CO_2 line list in the HITRAN2020 edition compared to the HITRAN2016 is given in **Table 2**. The HITRAN2020 carbon dioxide line list generated in HITRAN format is available on the HITRANonline website www.hitran.org. and Supplementary material of this paper. An overview of the line lists in HITRAN2020 and HITRAN2016 is plotted in **Fig.17.**

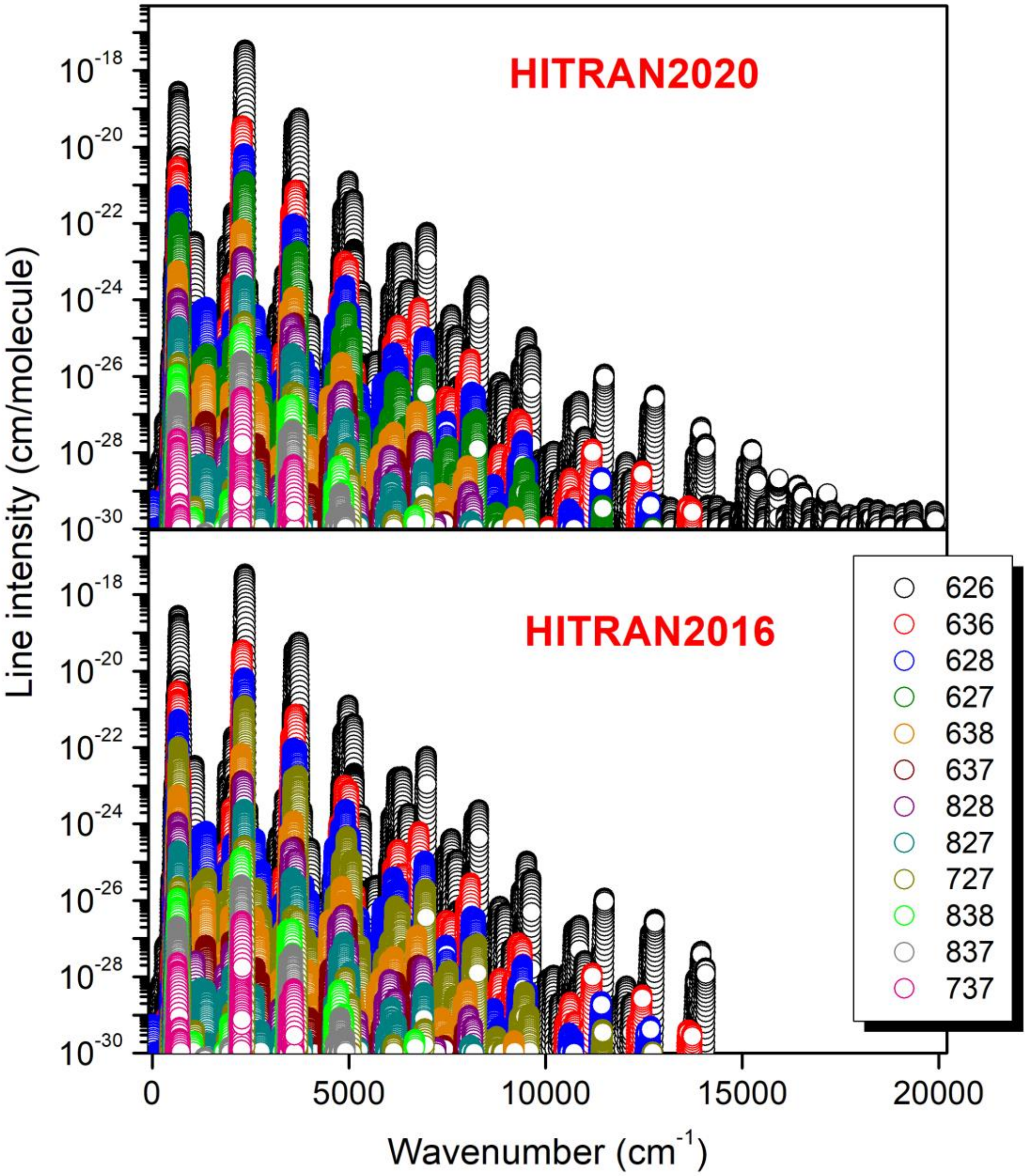


Fig. 17. An overview of the HITRAN2016 and HITRAN2020 line lists for the 12 stable CO_2 isotopologues: $^{12}C^{16}O_2$(626), $^{13}C^{16}O_2$(636), $^{16}O^{12}C^{18}O$(628), $^{16}O^{12}C^{17}O$(627), $^{16}O^{13}C^{18}O$(638), $^{16}O^{13}C^{17}O$(637), $^{12}C^{18}O_2$ (828), $^{18}O^{12}C^{17}O$(827), $^{12}C^{17}O_2$(727), $^{13}C^{18}O_2$(838), $^{18}O^{13}C^{17}O$(837), and $^{13}C^{17}O_2$(737) (The numbers in parentheses are the AFGL shorthand code for the isotopologues).

Table 2. Comparison of HITRAN2020 and HITRAN2016 line lists for the 12 stable CO_2 isotopologues.

Formula	AFGL code	Abundance	HITRAN2016			HITRAN2020		
			Number of lines	Spectral region (cm^{-1})	Q(296K)	Number of lines	Spectral region (cm^{-1})	Q(296K)
$^{12}C^{16}O_2$	626	0.984204	173024	158.302-14075.298	286.094	174446	158.302-19908.186	286.094
$^{13}C^{16}O_2$	636	0.011057	70577	332.649-13734.963	576.644	69870	332.649-13734.963	576.644
$^{16}O^{12}C^{18}O$	628	0.003947	127850	1.473-12677.181	607.713	122140	1.473-12677.182	607.713
$^{16}O^{12}C^{17}O$	627	7.339890×10^{-4}	77941	0.757-12726.562	3542.610	73942	0.757-12726.562	3542.610
$^{16}O^{13}C^{18}O$	638	4.434460×10^{-5}	43782	2.945-9212.609	1225.270	41058	2.945-9212.608	1225.270
$^{16}O^{13}C^{17}O$	637	8.246230×10^{-6}	25175	9.086-8061.741	7140.024	23607	9.086-8061.739	7140.024
$^{12}C^{18}O_2$	828	3.957340×10^{-6}	10522	482.813-8162.743	323.424	10498	482.814-8162.752	323.424
$^{17}O^{12}C^{18}O$	728	1.471800×10^{-6}	15878	491.181-8193.172	3766.044	14623	498.617-8193.172	3766.044
$^{12}C^{17}O_2$	727	1.368470×10^{-7}	6518	535.384-6932.693	10971.91	6493	535.384-6932.693	10971.91
$^{13}C^{18}O_2$	838	4.446000×10^{-8}	2916	539.626-6686.983	652.242	2926	539.620-6686.983	652.242
$^{17}O^{13}C^{18}O$	738	1.653540×10^{-8}	4190	549.473-4914.496	7593.900	3980	549.473-4914.496	7593.900
$^{13}C^{17}O_2$	737	1.537500×10^{-9}	1501	575.853-3614.084	22129.96	1501	575.853-3614.084	22129.96
Total			559874			545084		

Note: AFGL code is the shorthand notation for the isotopologue, abundance is the terrestrial value assumed by HITRAN, and *Q*(296 K) is the partition sum at the reference temperature of 296 K.

9. Conclusion

This work presents an improved and extended version of the HITRAN2020 spectroscopic database for the carbon dioxide molecule. The database includes updates of the line positions and intensities described in this work, and line shape parameters (described in Hashemi et al. [13]) for 12 stable CO_2 isotopologues. Critical validation tests for the spectroscopic data, including the comparisons with the most advanced theoretical and semi-empirical databases [17,18,23,27] and accurate experimental measurements, were carried out. Evaluation of the HITRAN CO_2 line lists by comparison to laboratory and atmospheric spectra below 8310 cm^{-1} and the description of the updates made for the bands having mixed CDSD and UCL-IAO line intensities in the HITRAN2016 line list below 8000 cm^{-1} are presented. Recent experimental measurements with sub-percent uncertainty [19–22] were used to improve the CO_2 bands in the (1.4-2.1) µm region. Several new CO_2 bands (more than 3600 transitions) above 8000 cm^{-1} were added to the HITRAN2020 edition from the new high-temperature UCL-4000 $^{12}C^{16}O_2$ line list from the ExoMol [18]database. Also, the updated CO_2 line list has been extended by including new experimentally observed bands [14] corresponding to the $^{16}O^{12}C^{18}O$ isotopologue. The magnetic dipole 01111-00001 band of the $^{12}C^{16}O_2$ isotopologue in the 3.3 µm region was introduced into HITRAN for the first time. Updated self- and air-broadened line shape parameters of CO_2, as described in Ref. [13] and involved in the enhancement of the HITRAN databases, were also revised. These updates of the CO_2 line parameters in HITRAN2020 are expected to have an important impact on the capabilities of current and future remote-sensing missions. The updated line lists for 12 CO_2 isotopologues are available as Supplementary material of this paper or can be downloaded from the HITRAN website (www.hitran.org).

Acknowledgments

This work was supported by NASA grant funding from AURA NNX17AI78G. The National Institute of Standards and Technology (NIST) received support from the NASA Science Team for the OCO Missions (NRA) NNH17ZDA001N-OCO2 and the NIST Greenhouse Gas and Climate Science Measurements Program. This work was also supported by the Ministry of Science and Higher Education of the Russian Federation. The work performed at UCL was supported by the STFC Projects No. ST/M001334/1 and ST/R000476/1. Part of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with NASA.

References

[1] Butz A, Guerlet S, Hasekamp O, Schepers D, Galli A, Aben I, et al. Toward accurate CO_2 and CH_4 observations from GOSAT. Geophysical Research Letters 2011;38:2–7. https://doi.org/10.1029/2011GL047888.

[2] Alexe M, Bergamaschi P, Segers A, Detmers R, Butz A, Hasekamp O, et al. Inverse modelling of CH_4 emissions for 2010-2011 using different satellite retrieval products from GOSAT and SCIAMACHY. Atmospheric Chemistry and Physics 2015;15:113–33. https://doi.org/10.5194/acp-15-113-2015.

[3] Yokota T, Yoshida Y, Eguchi N, Ota Y, Tanaka T, Watanabe H, et al. Global Concentrations of CO_2 and CH_4 Retrieved from GOSAT : First Preliminary Results. Scientific Online Letters on the Atmosphere 2009;5:160–3. https://doi.org/ 10.2151/sola.2009–041.

[4] Nakajima, M., Suto, H., Yotsumoto, K., Abe, M., Kuze, A., Shiomi, K. et al. Overview of the GOSAT-2 Mission, Proceedings of the 29th ISTS Nagoya-Aichi, Japan 2013:60.

[5] Fabiano Oyafuso, Vivienne H.Payne,Brian J.Drouin,V. Malathy Devi, D. Chris Benner. High accuracy absorption coefficients for the Orbiting Carbon Observatory-2 (OCO-2) mission: Validation of updated carbon dioxide cross-sections using atmospheric spectra. Journal of Quantitative Spectroscopy and Radiative Transfer 2017;203:213–23. https://doi.org/https://doi.org/10.1016/j.jqsrt.2017.06.012.

[6] Eldering, A., Wennberg, P. O., Crisp, D., Schimel, D. S., Gunson, M. R., Chatterjee, A. et al. The Orbiting Carbon Observatory-2 early science investigations of regional carbon dioxide fluxes. Science 2017;358:188. https://doi.org/10.1126/science.aam5745.

[7] Eldering A, Taylor TE, O’Dell CW, Pavlick R. The OCO-3 mission: Measurement objectives and expected performance based on 1 year of simulated data. Atmospheric Measurement Techniques 2019;12:2341–70. https://doi.org/10.5194/amt-12-2341-2019.

[8] Fischer H, Birk M, Blom C, Carli B, Carlotti M, von Clarmann T, et al. MIPAS: An instrument for atmospheric and climate research. Atmospheric Chemistry and Physics 2008;8:2151–88. https://doi.org/10.5194/acp-8-2151-2008.

[9] Bernath PF, McElroy CT, Abrams MC, Boone CD, Butler M, Camy-Peyret C, et al. Atmospheric chemistry experiment (ACE): Mission overview. Geophysical Research Letters 2005;32:1–5. https://doi.org/10.1029/2005GL022386.

[10] Wunch D, Toon GC, Blavier JFL, Washenfelder RA, Notholt J, Connor BJ, et al. The total carbon column observing network. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 2011;369:2087–112. https://doi.org/10.1098/rsta.2010.0240.

[11] Hase F. Improved instrumental line shape monitoring for the ground-based, high-resolution FTIR spectrometers of the Network for the Detection of Atmospheric Composition Change. Atmospheric Measurement Techniques 2012;5:603–10. https://doi.org/10.5194/amt-5-603-2012.

[12] Gordon IE, Rothman LS, Hill C, Kochanov RV, Tan Y, Bernath PF, et al. The HITRAN2016 molecular spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer 2017;203:3–69. https://doi.org/10.1016/j.jqsrt.2017.06.038.

[13] Hashemi R, Gordon IE, Tran H, Kochanov RV, Karlovets EV, Tan Y, Lamouroux J, et al. Revising the line-shape parameters for air- and self- broadened CO_2 lines toward a sub-percent accuracy level. JQSRT 2020;256:107283. https://doi.org/https://doi.org/10.1016/j.jqsrt.2020.107283.

[14] Karlovets EV, Kassi S, Campargue A. Journal of Quantitative Spectroscopy & Radiative Transfer High sensitivity CRDS of CO_2 in the 1.18 µm transparency window . Validation tests of current spectroscopic databases 2020;247:1–8. https://doi.org/10.1016/j.jqsrt.2020.106942.

[15] Toon GC. CO_2 Spectroscopy Evaluation: 670 to 8310 cm^{-1}, Reports and Presentations for the HITRAN meeting, Jun 2020, Jet Propulsion Laboratory, California Institute of Technology (2020).

[16] Toon GC. CO_2 Spectroscopy Evaluation: 670 to 7000 cm^{-1} , Reports and Presentations for the ACE STM, Oct 2018, Jet Propulsion Laboratory, California Institute of Technology (2018).

[17] Tashkun SA, Perevalov VI, Gamache RR, Lamouroux J. CDSD-296, high-resolution carbon dioxide spectroscopic databank: An update. Journal of Quantitative Spectroscopy and Radiative Transfer 2019;228:124–31. https://doi.org/10.1016/j.jqsrt.2019.03.001.

[18] Yurchenko SN, Mellor TM, Freedman RS, Tennyson J. ExoMol line lists-XXXIX. Ro-vibrational molecular line list for CO_2. Monthly Notices of the Royal Astronomical Society 2020;496:5282–91. https://doi.org/10.1093/mnras/staa1874.

[19] Long DA, Reed ZD, Fleisher AJ, Mendonca J, Roche S, Hodges JT. High-Accuracy Near-Infrared Carbon Dioxide Intensity Measurements to Support Remote Sensing. Geophysical Research Letters 2020;47:e2019GL086344. https://doi.org/10.1029/2019GL086344.

[20] Fleurbaey H, Yi H, Adkins EM, Fleisher AJ, Hodges JT. Cavity ring-down spectroscopy of CO_2 near λ = 2.06 µm: Accurate transition intensities for the Orbiting Carbon Observatory-2 (OCO-2) "strong band." Journal of Quantitative Spectroscopy and Radiative Transfer 2020;252:107104. https://doi.org/10.1016/j.jqsrt.2020.107104.

[21] Birk M, Röske C, Wagner C. Measurement and line parameter database CO_2 6000-7000 cm^{-1}, Zenodo 2021.

[22] Birk M, Röske C, Wagner C. High accuracy CO_2 Fourier transform measurements in the range 6000–7000 cm^{-1}. Journal of Quantitative Spectroscopy and Radiative Transfer Submitted to HITRAN2020 Special Issue 2021.

[23] Huang X, Richard S. Freedman B, Lee TJ. Ames-2016 line lists for 13 isotopologues of CO_2: Updates, consistency, and remaining issues. Journal of Quantitative Spectroscopy and Radiative Transfer 2017;203:224–41. https://doi.org/10.1016/j.jinf.2020.02.020.

[24] Gordon IE, Rothman LS, Hargreaves, Hashemi R, Karlovets EV, Skinner FM, Conway EK, Hill C, et al. The HITRAN2020 molecular spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer Submitted to HITRAN2020 Special Issue 2021.

[25] Hill C, Gordon IE, Kochanov RV, Barrett L, Wilzewski JS, Rothman LS. HITRANonline: An online interface and the flexible representation of spectroscopic data in the HITRAN database. Journal of Quantitative Spectroscopy and Radiative Transfer 2016;177:4–14. https://doi.org/10.1016/j.jqsrt.2015.12.012.

[26] Tashkun SA, Perevalov VI, Gamache RR, Lamouroux J. CDSD-296, high resolution carbon dioxide spectroscopic databank: Version for atmospheric applications. Journal of Quantitative Spectroscopy and Radiative Transfer 2015;152:45–73. https://doi.org/10.1016/j.jqsrt.2014.10.017.

[27] Zak E, Tennyson J, Polyansky OL, Lodi L, Zobov NF, Tashkun SA, et al. A room temperature CO_2 line list with ab initio computed intensities. Journal of Quantitative Spectroscopy and Radiative Transfer 2016;177:31–42. https://doi.org/10.1016/j.jqsrt.2015.12.022.

[28] Zak EJ, Tennyson J, Polyansky OL, Lodi L, Zobov NF, Tashkun SA, et al. Room temperature linelists for CO_2 asymmetric isotopologues with ab initio computed intensities. Journal of Quantitative Spectroscopy and Radiative Transfer 2017;203:265–81. https://doi.org/10.1016/j.jqsrt.2017.01.037.

[29] Zak EJ, Tennyson J, Polyansky OL, Lodi L, Zobov NF, Tashkun SA, et al. Room temperature linelists for CO_2 symmetric isotopologues with ab initio computed intensities. Journal of Quantitative Spectroscopy and Radiative Transfer 2017;189:267–80. https://doi.org/10.1016/j.jqsrt.2015.12.022.

[30] Teffo JL, Sulakshina ON, Perevalov VI. Effective Hamiltonian for rovibrational energies and line intensities of carbon dioxide. Journal of Molecular Spectroscopy 1992;156:48–64. https://doi.org/10.1016/0022-2852(92)90092-3.

[31] Teffo JL, Lyulin OM, Perevalov VI, Lobodenko EI. Application of the effective operator approach to the calculation of $^{12}C^{16}O_2$ line intensities. Journal of Molecular Spectroscopy 1998;187:28–41. https://doi.org/10.1006/jmsp.1997.7455.

[32] Polyansky OL, Bielska K, Ghysels M, Lodi L, Zobov NF, Hodges JT, et al. High-Accuracy CO_2 Line Intensities Determined from Theory and Experiment. Physical Review Letters 2015;114:1–5. https://doi.org/10.1103/PhysRevLett.114.243001.

[33] Yurchenko SN, Thiel W, Jensen P. Theoretical ROVibrational Energies (TROVE): A robust numerical approach to the calculation of rovibrational energies for polyatomic molecules. Journal of Molecular Spectroscopy 2007;245:126–40. https://doi.org/10.1016/j.jms.2007.07.009.

[34] Chris Benner, V. Malathy Devi, Curtis P. Rinsland and Penelope S. Ferry-Leeper. Absolute intensities of CO_2 lines in the 3140–3410-cm^{-1} spectral region. Applied Optics 1988;27:1588–97. https://doi.org/https://doi.org/10.1364/AO.27.001588.

[35] Toth RA, Brown LR, Miller CE, Devi VM, Benner DC. Spectroscopic database of CO_2 line parameters: 4300–7000 cm^{-1}. Journal of Quantitative Spectroscopy and Radiative Transfer 2008;109:906–21. https://doi.org/10.1016/j.jqsrt.2007.12.004.

[36] Tomoaki Tanaka, Masashi Fukabori, Takafumi Sugita, Hideaki Nakajima et al. Spectral line parameters for CO_2 bands in the 4.8- to 5.3-µm region. Journal of Molecular Spectroscopy 2006;239:1–10. https://doi.org/https://doi.org/10.1016/j.jms.2006.05.013.

[37] Rinsland CP, Benner DC, Devi VM. Measurements of absolute line intensities in carbon dioxide bands near 5.2 µm. Applied Optics 1985;24:1644. https://doi.org/10.1364/ao.24.001644.

[38] Karlovets EV, Kassi S, Tashkun SA, Perevalov VI, Campargue A. High sensitivity Cavity Ring Down spectroscopy of carbon dioxide in the 1.19-1.26μm region. Journal of Quantitative Spectroscopy and Radiative Transfer 2014;144:137-153. https://doi.org/10.1016/j.jqsrt.2014.04.001.

[39] Čermák P, Karlovets EV, Mondelain D, Kassi S, Perevalov VI, Campargue A. High sensitivity CRDS of CO_2 in the 1.74 µm transparency window. A validation test for the spectroscopic databases. Journal of Quantitative Spectroscopy and Radiative Transfer 2018;207:95–103. https://doi.org/10.1016/j.jqsrt.2017.12.018.

[40] Karlovets EV, Čermák P, Mondelain D, Kassi S, Campargue A, Tashkun SA, et al. Analysis and theoretical modeling of the ^{18}O enriched carbon dioxide spectrum by CRDS near 1.74 µm. Journal of Quantitative Spectroscopy and Radiative Transfer 2018;217:73–85. https://doi.org/10.1016/j.jqsrt.2018.05.017.

[41] Rinsland CP, Benner DC. Absolute intensities of spectral lines in carbon dioxide bands near 2050 cm^{-1}. Applied Optics 1984;23:4523–8. https://doi.org/https://doi.org/10.1364/AO.23.004523.

[42] Rinsland CP, Benner DC and Devi VM. Absolute line intensities in CO_2 bands near 4.8 µm. Applied Optics 1986;25:1204–14. https://doi.org/https://doi.org/10.1364/AO.25.001204.

[43] Rothman LS, Gordon IE, Barbe A, Benner DC, Bernath PF, Birk M, et al. The HITRAN 2008 molecular spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer 2009;110:533–72. https://doi.org/10.1016/j.jqsrt.2009.02.013.

[44] Rothman LS, Gordon IE, Babikov Y, Barbe A, Chris Benner D, Bernath PF, et al. The HITRAN2012 molecular spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer 2013;130:4–50. https://doi.org/10.1016/j.jqsrt.2013.07.002.

[45] Wunch D, Toon GC, Blavier JFL, Washenfelder RA, Notholt J, Connor BJ, et al. GFIT. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 2011;369:2087–112. https://doi.org/10.1098/rsta.2010.0240.

[46] Karlovets EV, Sidorenko AD, Mondelain D, Kassi S, Campargue A, Sidorenko AD, et al. The $^{13}CO2$ absorption spectrum by CRDS near 1.74 µm. Journal of Molecular Spectroscopy 2018;354:54–9. https://doi.org/10.1016/j.jms.2018.10.003.

[47] Lawrence P.Giver, Linda R.Brown, Charles Chackerian, Richard S. Freedman. The rovibrational intensities of five absorption bands of $^{12}C^{16}O_2$ between 5218 and 5349 cm^{-1}. Journal of Quantitative Spectroscopy and Radiative Transfer 2003;78:417–36. https://doi.org/10.1016/S0022-4073(02)00277-7.

[48] Perevalov BV, Kassi S, Romanini D, Perevalov VI, Tashkun SA, Campargue A. CW-cavity ringdown spectroscopy of carbon dioxide isotopologues near 1.5 µm. Journal of Molecular Spectroscopy 2006;238:241–55. https://doi.org/10.1016/j.jms.2006.05.009.

[49] Miller CE, Crisp D, DeCola PL, Olsen SC, Randerson JT, Michalak AM, et al. Precision requirements for space-based XCO_2 data. Journal of Geophysical Research Atmospheres 2007;112:1–19. https://doi.org/10.1029/2006JD007659.

[50] Campbell JF, Lin B, Dobler J, Pal S, Davis K, Erxleben W, McGregor D, O'Dell C, Bell E, et al. Field Evaluation of Column CO_2 Retrievals From Intensity-Modulated Continuous-Wave Differential Absorption Lidar Measurements During the ACT-America Campaign. Earth and Space Science 2020;7:e2019EA000847. https://doi.org/10.1029/2019EA000847.

[51] Tennyson J, Yurchenko SN, Al-Refaie AF, Clark VHJ, Chubb KL, Conway EK, Dewan A, Gorman MN, Hill C, et al. The 2020 release of the ExoMol database: molecular line lists for exoplanet and other hot atmospheres. Journal of Quantitative Spectroscopy and Radiative Transfer 2020; 255, 107228. https://doi.org/ 10.1016/j.jqsrt.2020.107228.

[52] Rothman LS, Hawkins RL, Wattson RB, Gamache RR. Energy levels, intensities, and linewidths of atmospheric carbon dioxide bands. Journal of Quantitative Spectroscopy and Radiative Transfer 1992;48:537–66. https://doi.org/10.1016/0022-4073(92)90119-O.

[53] Trokhimovskiy A, Perevalov V, Korablev O, Fedorova A, Olsen KS, Bertaux JL, et al. First observation of the magnetic dipole CO_2 main isotopologue absorption band at 3.3 µm in the atmosphere of Mars by the ExoMars Trace Gas Orbiter ACS instrument. Astronomy & Astrophysics 2020;639:1–7. https://doi.org/10.1051/0004-6361/202038134.

[54] Korablev O, Montmessin F, Trokhimovskiy A, Fedorova AA, Shakun AV, Grigoriev AV, et al. The Atmospheric Chemistry Suite (ACS) of Three Spectrometers for the ExoMars 2016 Trace Gas Orbiter. Space Science Reviews 2018;214:7. https://doi.org/10.1007/s11214-017-0437-6.

[55] Perevalov VI, Trokhimovskiy AY, Lukashevskaya AA, Korablev OI, et al. Magnetic dipole and electric quadrupole absorption in carbon dioxide. Journal of Quantitative Spectroscopy and Radiative Transfer 2021;259:107408. https://doi.org/10.1016/j.jqsrt.2020.107408.

[56] Borkov YG, Solodov AM, Solodov AA, Perevalov VI. Line intensities of the 01111–00001 magnetic dipole absorption band of $^{12}C^{16}O_2$: Laboratory measurements. Journal of Molecular Spectroscopy 2021;376:111418. https://doi.org/https://doi.org/10.1016/j.jms.2021.111418.

[57] Majcherova Z, MacKo P, Romanini D, Perevalov VI, Tashkun SA, Teffo JL, et al. High-sensitivity CW-cavity ringdown spectroscopy of $^{12}CO_2$ near 1.5 µm. Journal of Molecular Spectroscopy 2005;230:1–21. https://doi.org/10.1016/j.jms.2004.09.011.

[58] Fleurbaey H, Grilli R, Mondelain D, Kassi S, Yachmenev A, Yurchenko SN, Campargue A. Electric-quadrupole and magnetic-dipole conitributions to the $\nu_2+\nu_3$ band of carbon dioxide near 3.3 µm. Journal of Quantitative Spectroscopy and Radiative Transfer 2021;266:107558. https://doi.org/10.1016/j.jqsrt.2021.107558.

[59] Rothman LS, Jacquemart D, Barbe A, Benner DC, Birk M, Brown LR, et al. The HITRAN 2004 molecular spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer 2005;96:139–204. https://doi.org/10.1016/j.jqsrt.2004.10.008.

[60] Yachmenev A, Küpper J, Campargue A, Yurchenko SN, and Tennyson. Quadrupole transitions in carbon dioxide. J Chem Physics, 2021 (in press).

[61] Voigt W. Über das Gesetz Intensitätsverteilung innerhalb der Linien eines Gasspektrums. München; Berlin: Sitzber. Bayr Akad., 1912, 603 p.

[62] Hashemi R, Rozario H, Ibrahim A, Predoi-Cross A. Line shape study of the carbon dioxide laser band. Can J Phys 2013;91(11):924–36. https://doi.org/10.1139/ cjp- 2013- 0051.

[63] Ma H, Sun M, Zha S, Liu Q, Cao Z, Huang Y et al. Temperature dependence of line parameters of CO_2 near 2.004 µm studied by tunable diode laser spectroscopy. Chin Phys B 2018;27(2):023301. https://doi.org/10.1088/1674-1056/27/2/023301.

[64] Predoi-Cross A, Liu W, Murphy R, Povey C, Gamache R, Laraia A et al. Measurement and computations for temperature dependences of self-broadened carbon dioxide transitions in the 30012-00001 and 30013-00001 bands. Journal of Quantitative Spectroscopy and Radiative Transfer 2010;111(9):1065–79. https://doi.org/10.1016/j.jqsrt.2010.01.003.

[65] Hartmann J-M. A simple empirical model for the collisional spectral shift of air-broadened CO_2 lines. Journal of Quantitative Spectroscopy and Radiative Transfer 2009;110(18):2019–26. https://doi.org/10.1016/j.jqsrt.2009.05.016.

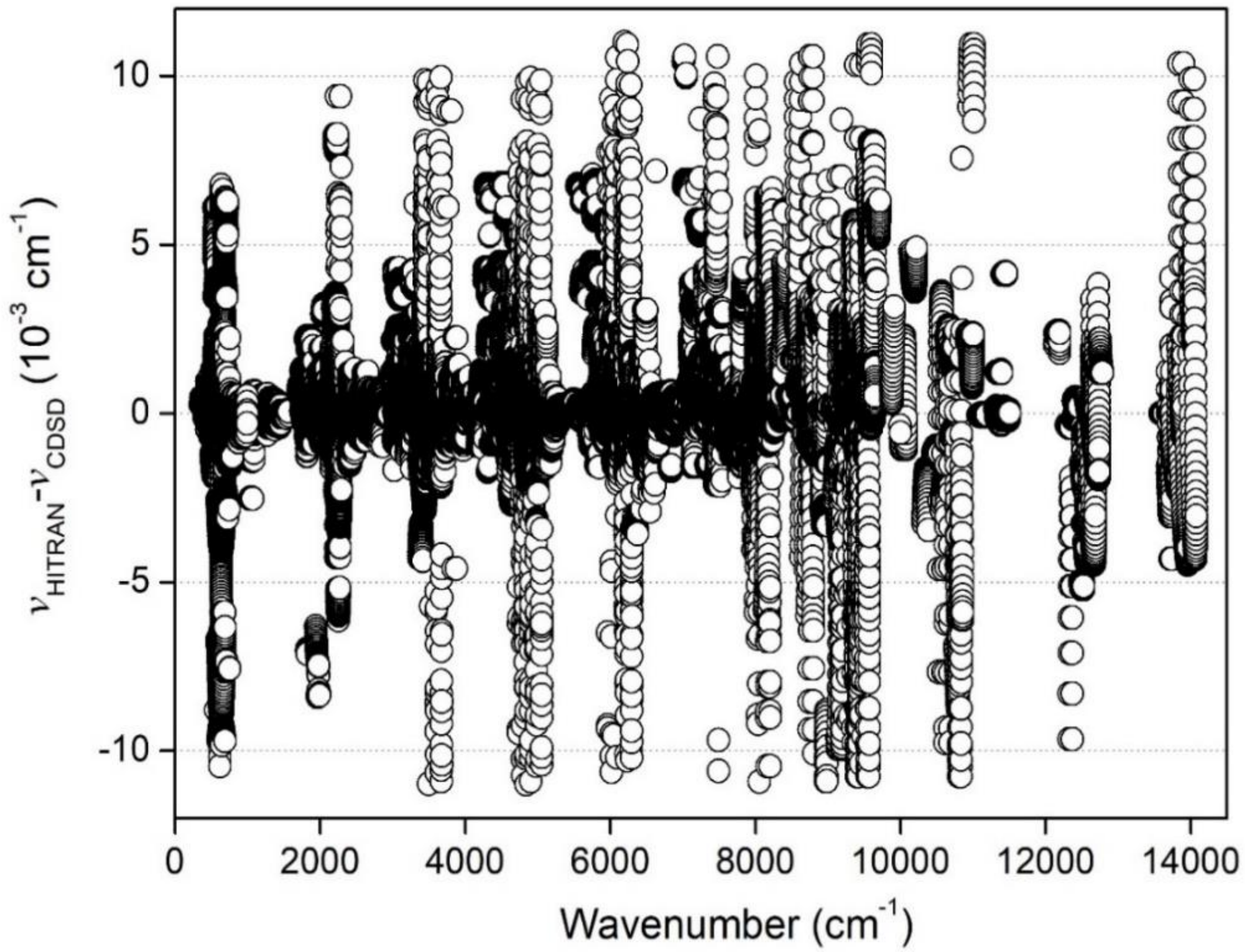
[66] Pickett HM. Effects of velocity averaging on the shapes of absorption lines. J Chem Phys 1980;73(12):6090–4. https://doi.org/10.1063/1.440145.

[67] Pine AS. Line shape asymmetries in Ar-broadened HF (v = 10) in the Dicke arrowing regime. J Chem Phys 1994;101(5):3444–52. https://doi.org/10.1063/1.467529.

[68] Kochanov RV, Gordon IE, Rothman LS, Wcisło P, Hill C, Wilzewski JS. HITRAN Application Programming Interface (HAPI): A comprehensive approach to working with spectroscopic data. Journal of Quantitative Spectroscopy and Radiative Transfer 2016;177:15–30. https://doi.org/10.1016/j.jqsrt.2016.03.005.

[69] Lamouroux J, Régalia L, Thomas X, Auwera JV, Gamache RR, Rothman LS, Gordon IE, Hartmann J-M. CO_2 Line-mixing database and software update and its tests in the 2.1 µm and 4.3 µm regions. Journal of Quantitative Spectroscopy and Radiative Transfer 2015;151:88–96. https://doi.org/10.1016/ j.jqsrt.2014.09.017.

Fig. 1.



$\nu_{HITRAN}-\nu_{CDSD}$ (10^{-3} cm^{-1})
10
5
0
-5
-10
0
2000
4000
6000
8000
10000
12000
14000
Wavenumber (cm^{-1})

Fig. 2.

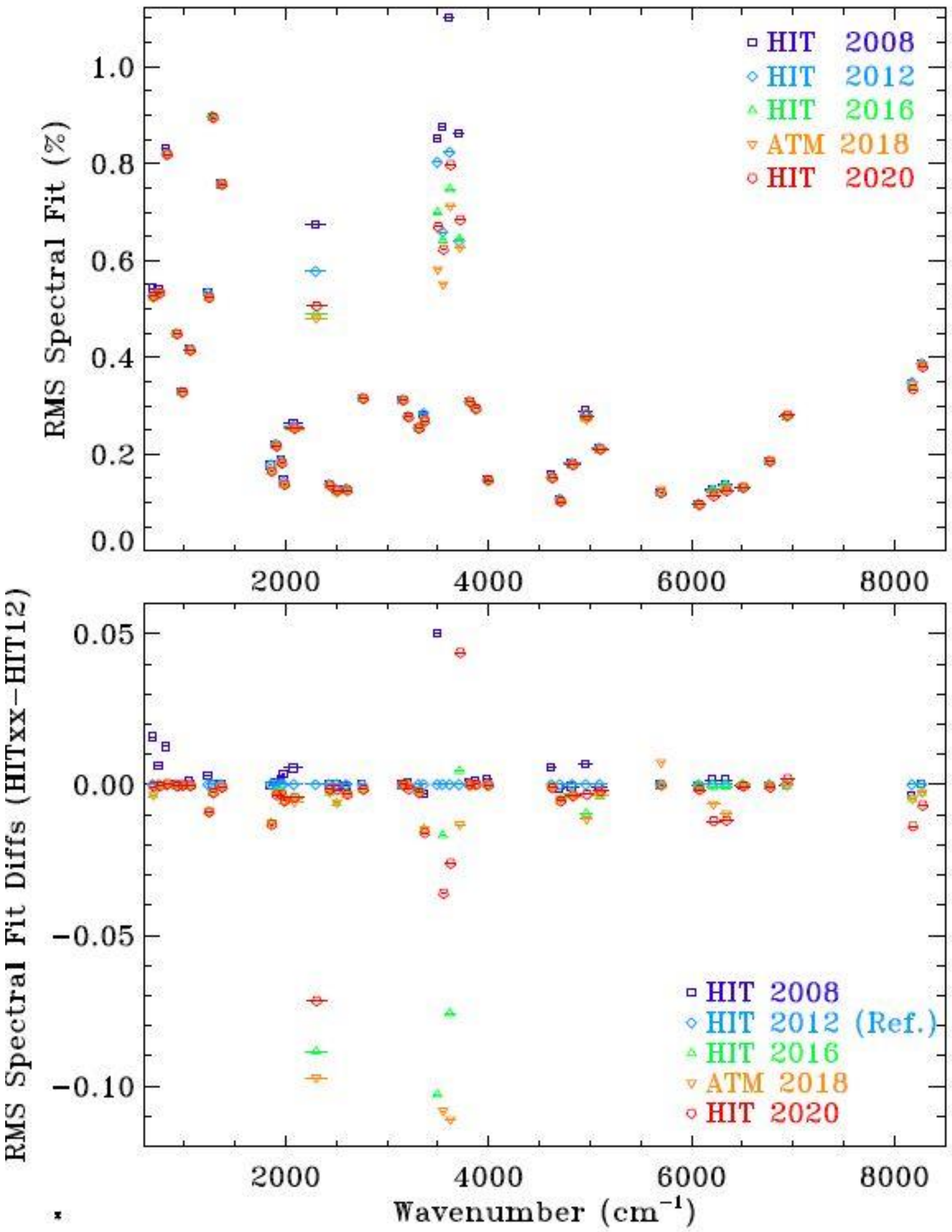
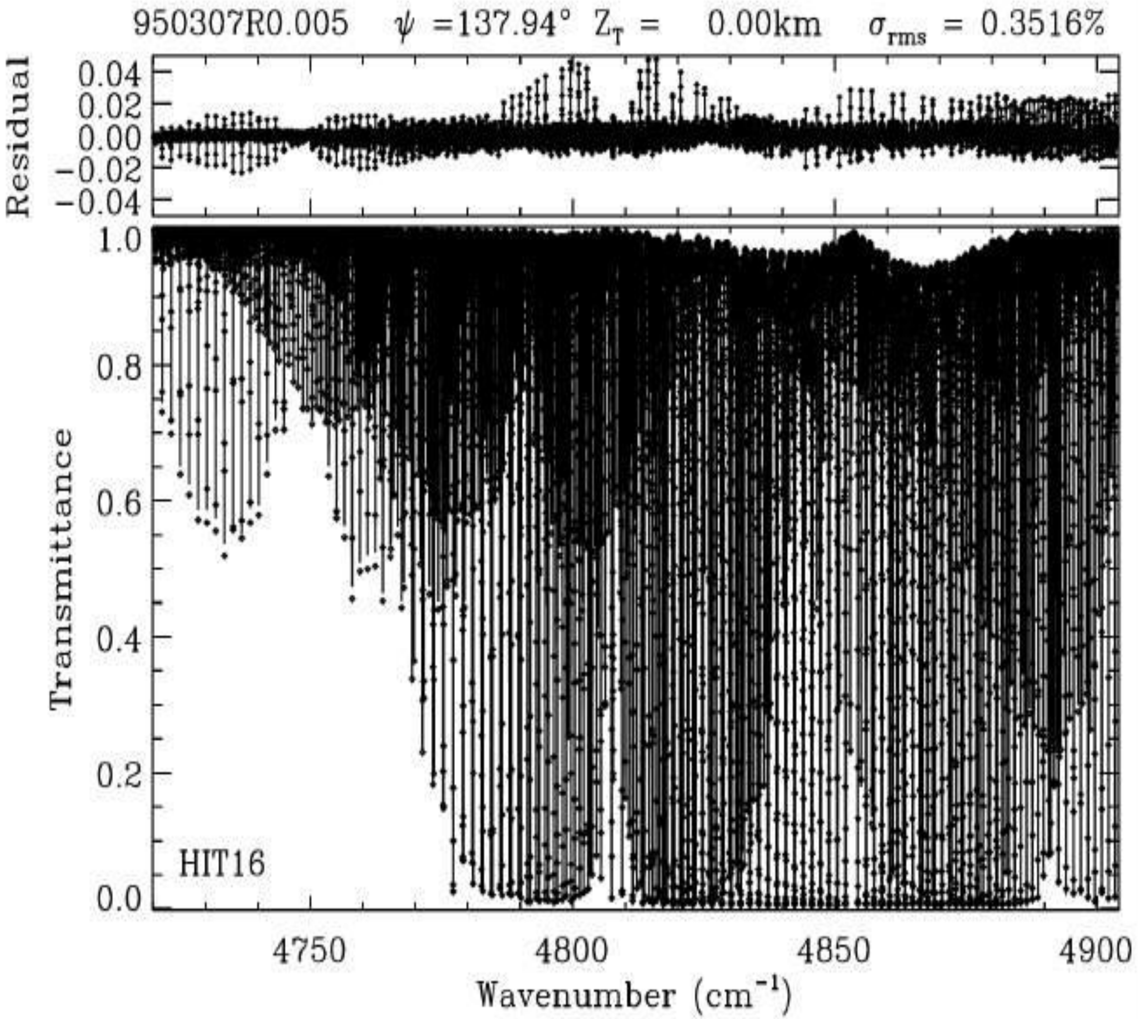
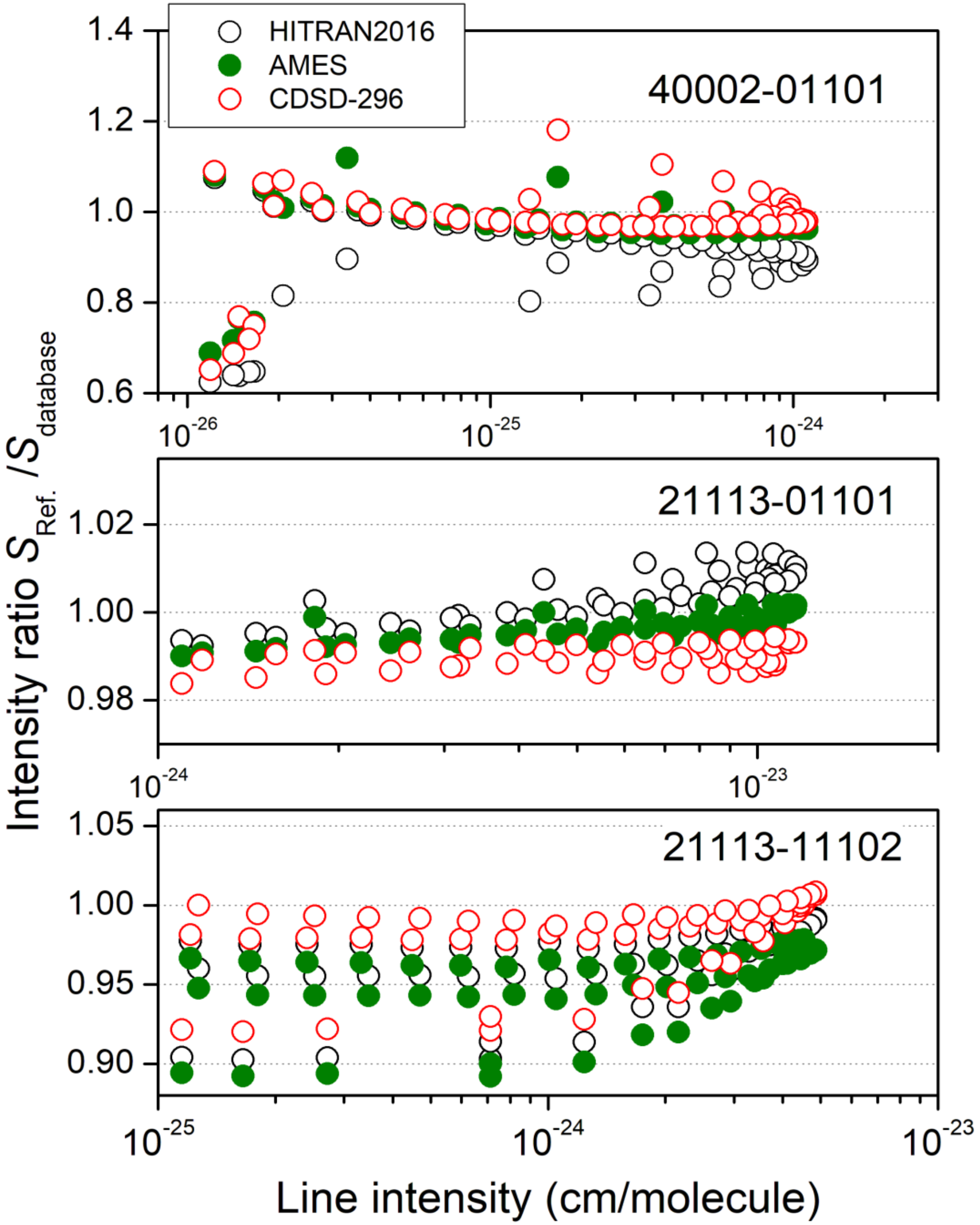

RMS Spectral Fit (%)
0.0
0.2
0.4
0.6
0.8
1.0
2000
4000
6000
8000
HIT 2008
HIT 2012
HIT 2016
ATM 2018
HIT 2020
RMS Spectral Fit Diffs (HITxx−HIT12)
0.05
0.00
−0.05
−0.10
HIT 2008
HIT 2012 (Ref.)
HIT 2016
ATM 2018
HIT 2020
Wavenumber (cm^{-1})

Fig. 3.



950307R0.005 ψ =137.94° Z_T = 0.00km σ_rms = 0.3516%
Residual
0.04
0.02
0.00
−0.02
−0.04
1.0
0.8
0.6
0.4
0.2
0.0
Transmittance
HIT16
4750
4800
4850
4900
Wavenumber (cm⁻¹)

Fig. 4.



○ HITRAN2016
● AMES
○ CDSD-296
40002-01101
21113-01101
21113-11102
Intensity ratio $S_{Ref.}/S_{database}$
Line intensity (cm/molecule)
1.4
1.2
1.0
0.8
0.6
10^{-26}
10^{-25}
10^{-24}
1.02
1.00
0.98
10^{-24}
10^{-23}
1.05
1.00
0.95
0.90
10^{-25}
10^{-24}
10^{-23}

Fig. 5.

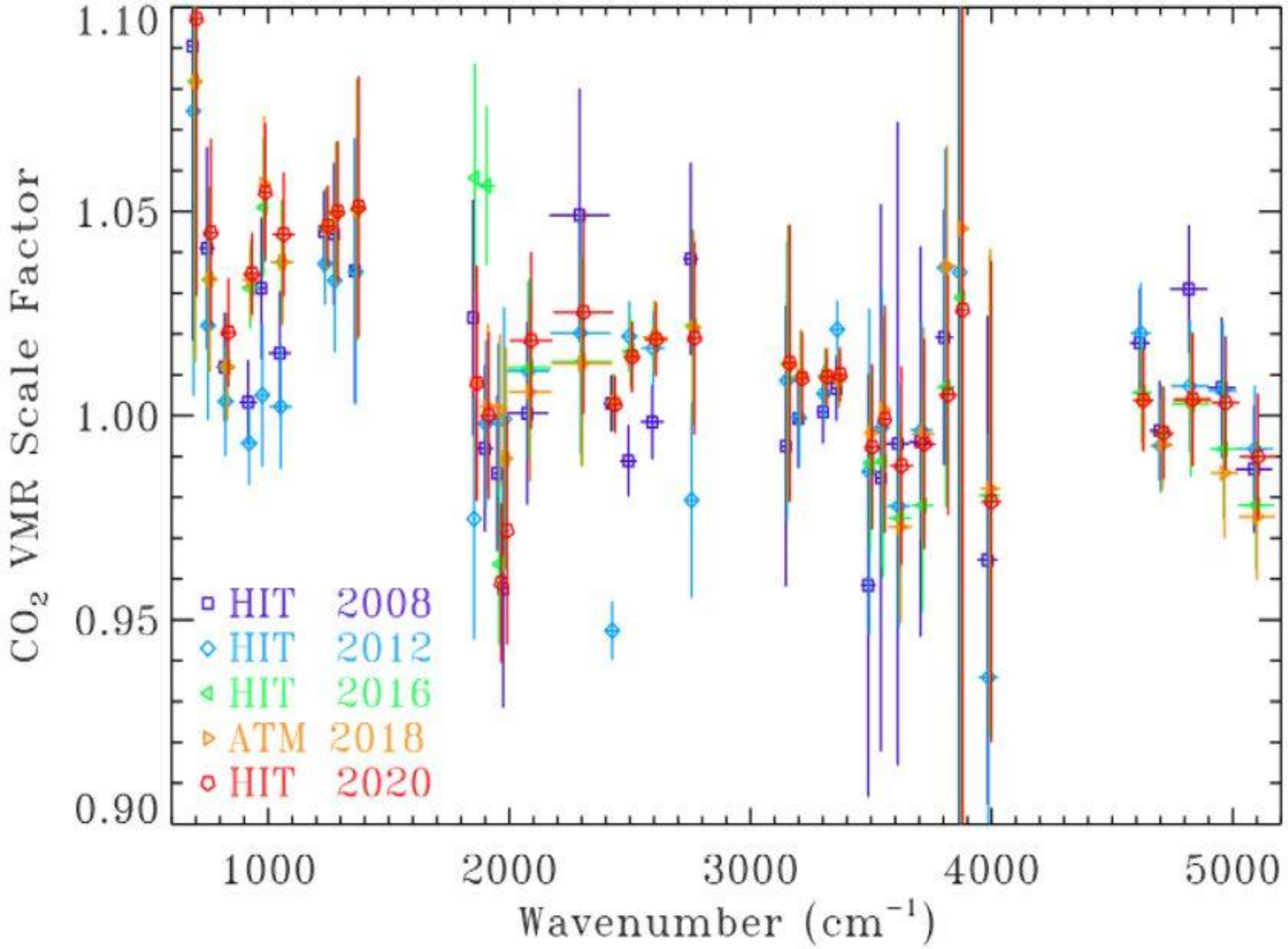

1.10
1.05
1.00
0.95
0.90
CO_2 VMR Scale Factor
1000
2000
3000
4000
5000
Wavenumber (cm^{-1})
□ HIT 2008
◇ HIT 2012
◁ HIT 2016
▷ ATM 2018
○ HIT 2020

Fig. 6.

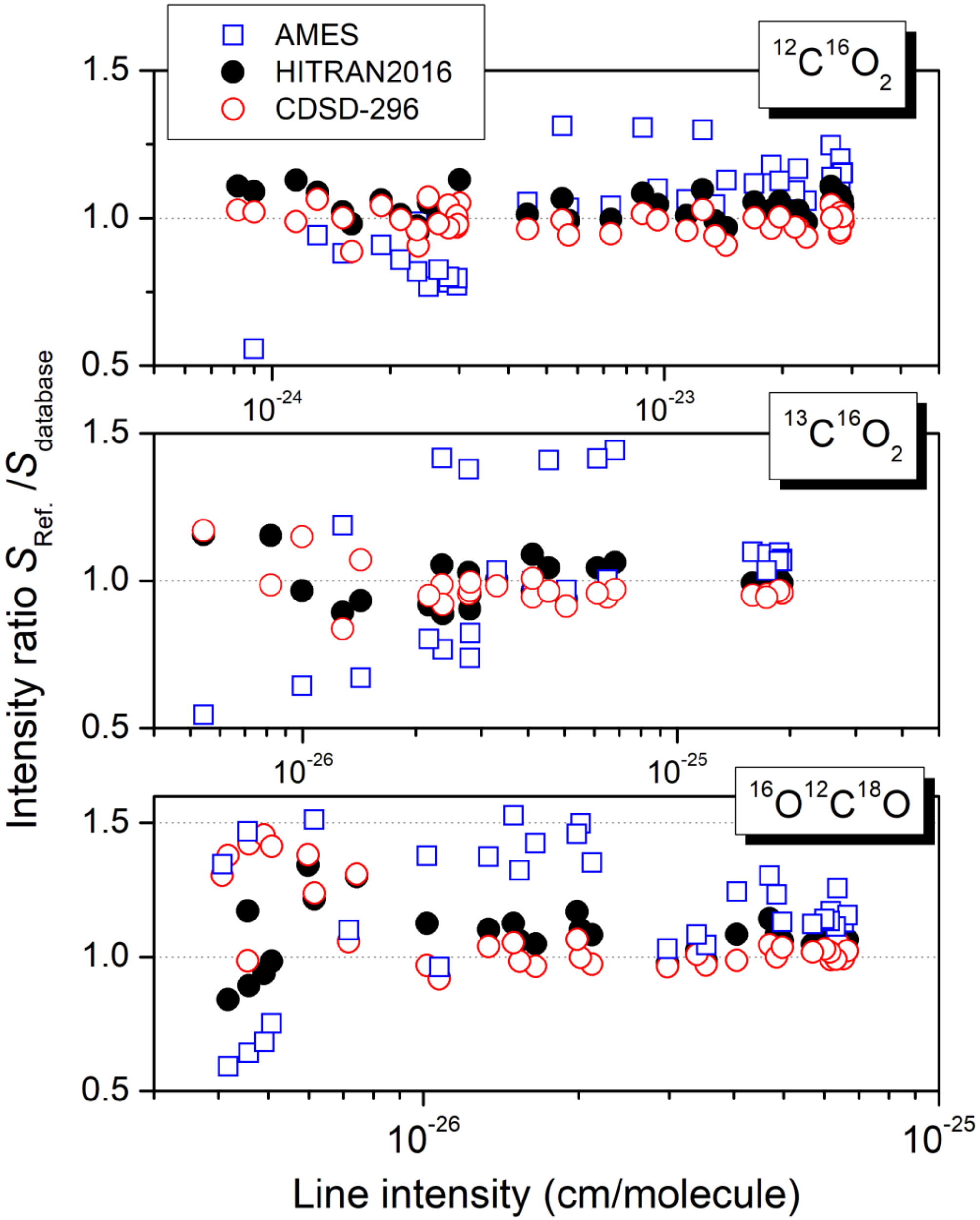
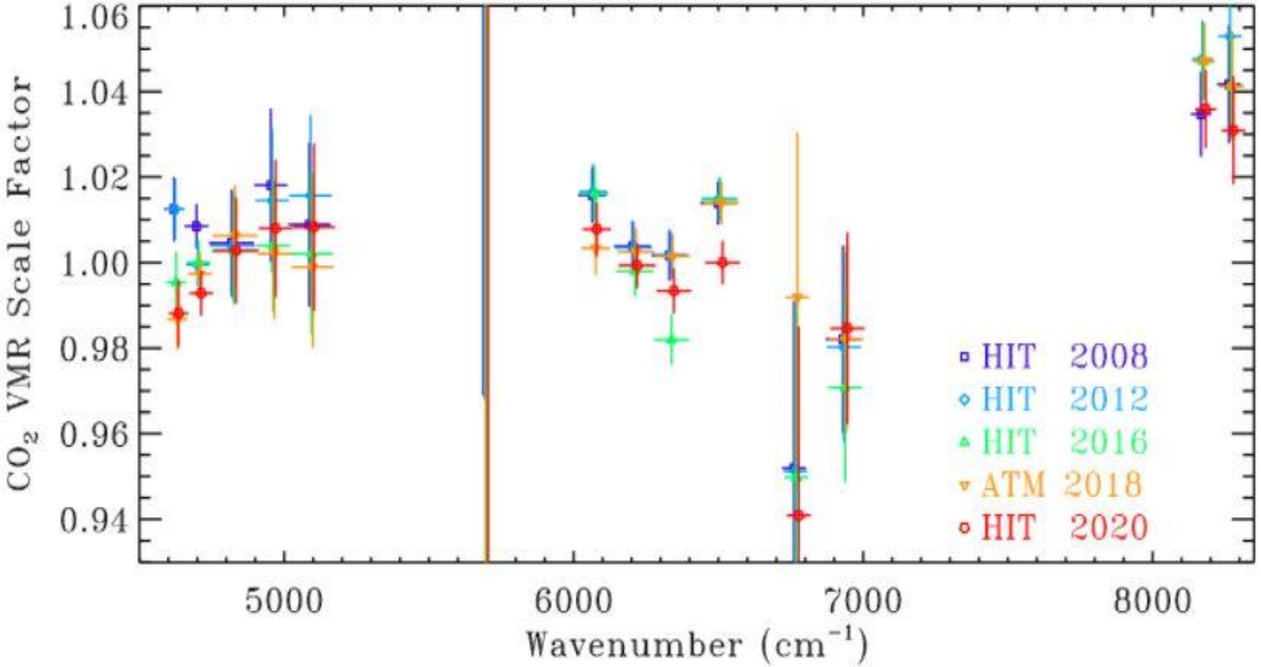

AMES
HITRAN2016
CDSD-296
$^{12}C^{16}O_2$
$^{13}C^{16}O_2$
$^{16}O^{12}C^{18}O$
Intensity ratio $S_{Ref.}/S_{database}$
1.5
1.0
0.5
10^{-24}
10^{-23}
10^{-26}
10^{-25}
Line intensity (cm/molecule)

Fig. 7.



1.06
1.04
1.02
1.00
0.98
0.96
0.94
CO_2 VMR Scale Factor
5000
6000
7000
8000
Wavenumber (cm^{-1})
□ HIT 2008
◇ HIT 2012
△ HIT 2016
▽ ATM 2018
○ HIT 2020

Fig. 8.

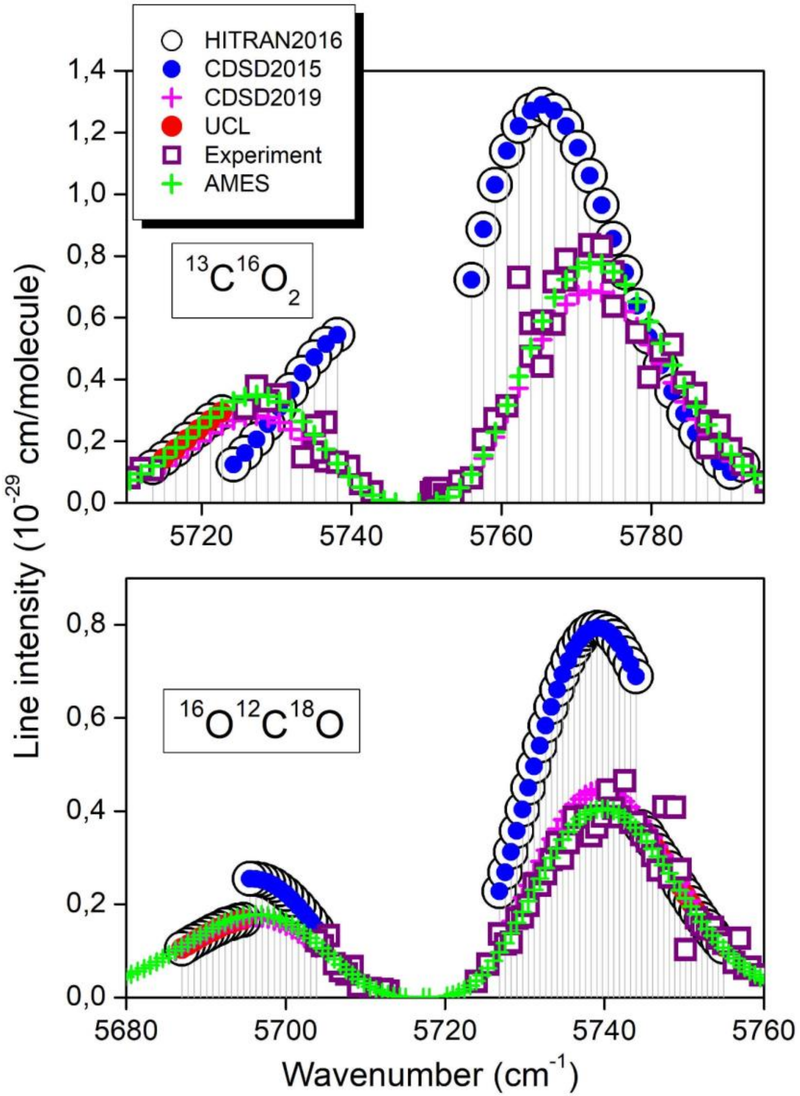

HITRAN2016
CDSD2015
CDSD2019
UCL
Experiment
AMES
$^{13}C^{16}O_2$
$^{16}O^{12}C^{18}O$
Line intensity (10^{-29} cm/molecule)
Wavenumber (cm^{-1})
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
5720
5740
5760
5780
5680
5700
5720
5740
5760

Fig. 9.

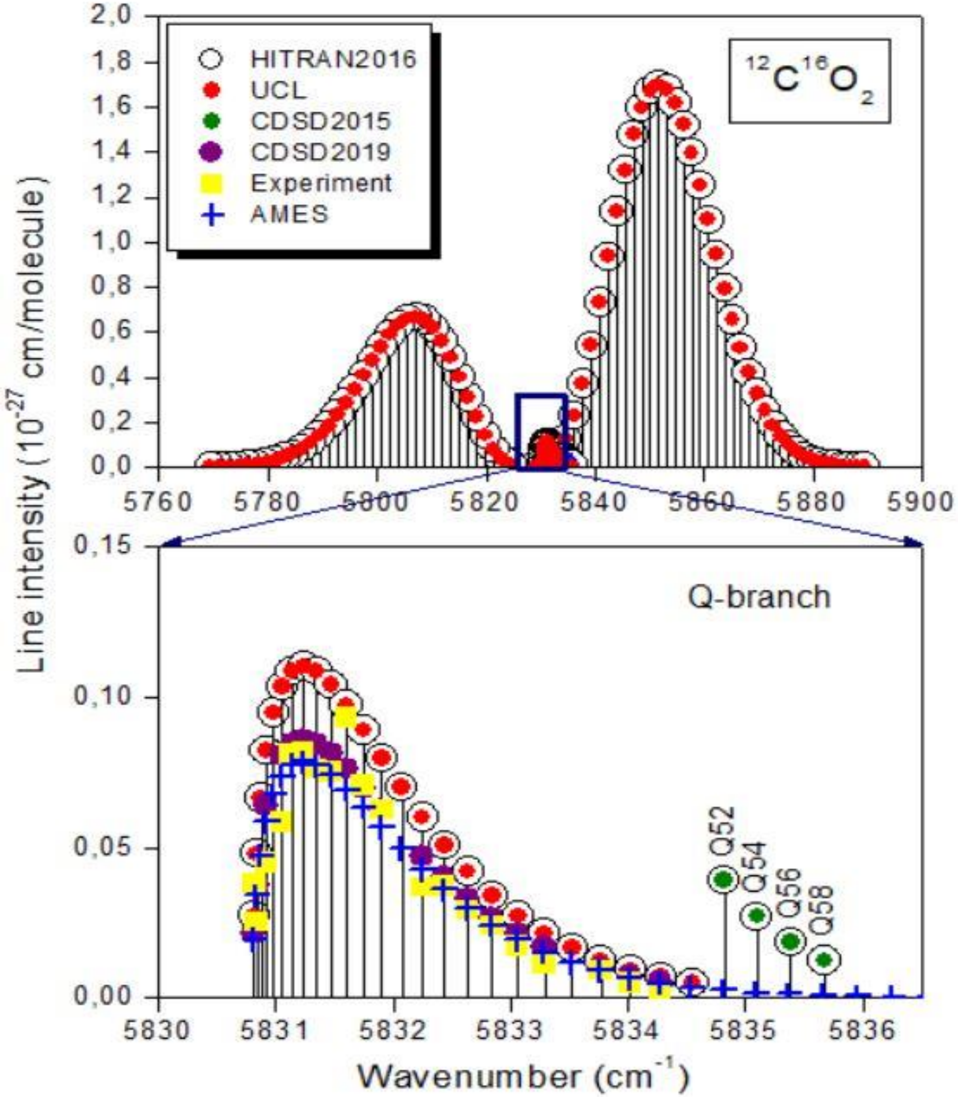
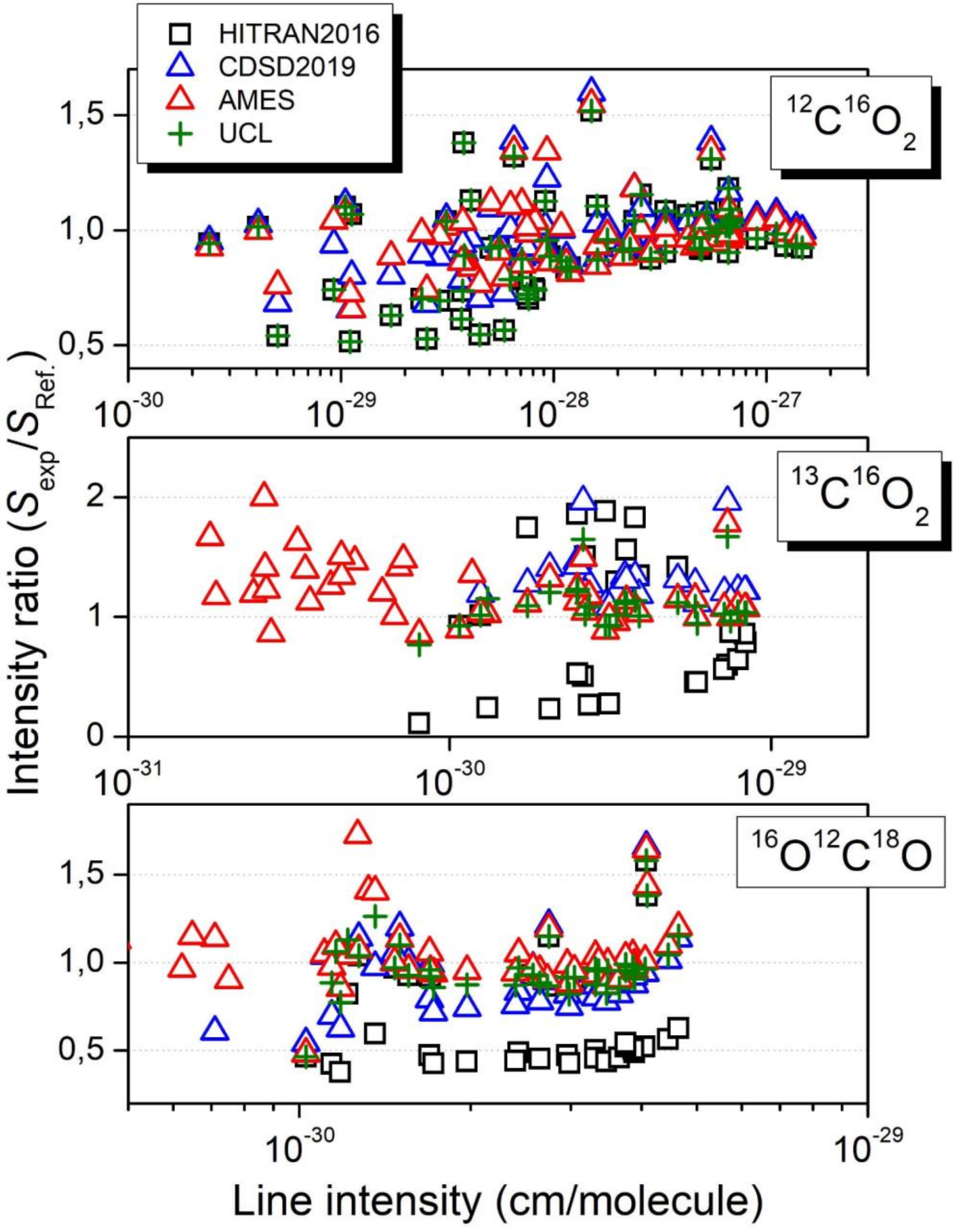

HITRAN2016
UCL
CDSD2015
CDSD2019
Experiment
AMES
$^{12}C^{16}O_2$
Line intensity (10^{-27} cm/molecule)
2,0
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
5760
5780
5800
5820
5840
5860
5880
5900
Q-branch
0,15
0,10
0,05
0,00
Q52
Q54
Q56
Q58
5830
5831
5832
5833
5834
5835
5836
Wavenumber (cm^{-1})

Fig. 10.



□ HITRAN2016
△ CDSD2019
△ AMES
+ UCL
$^{12}C^{16}O_2$
$^{13}C^{16}O_2$
$^{16}O^{12}C^{18}O$
Intensity ratio ($S_{exp}/S_{Ref.}$)
Line intensity (cm/molecule)
1,5
1,0
0,5
10^{-30}
10^{-29}
10^{-28}
10^{-27}
2
1
0
10^{-31}
10^{-30}
10^{-29}
1,5
1,0
0,5
10^{-30}
10^{-29}

Fig. 11.

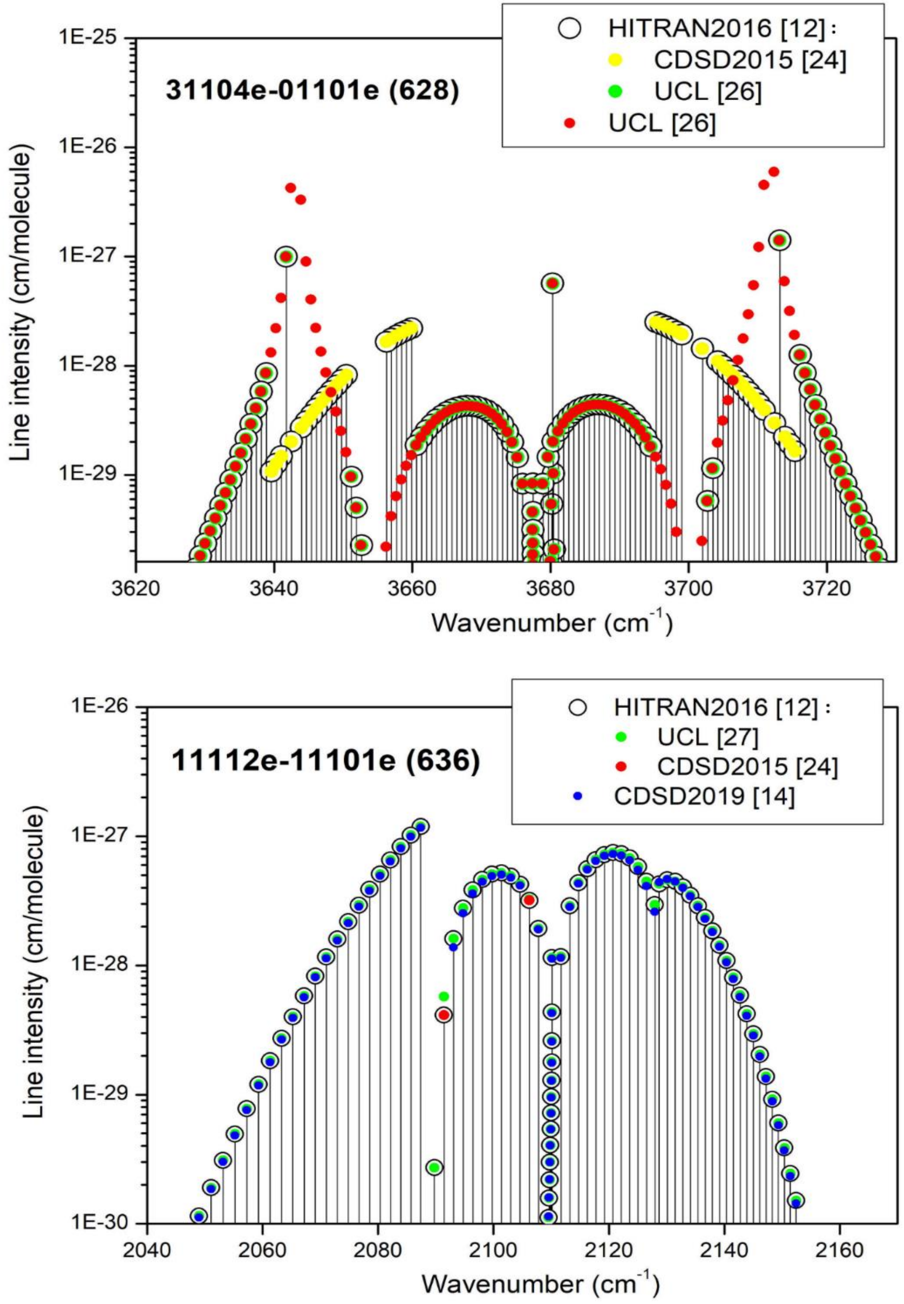

31104e-01101e (628)
○ HITRAN2016 [12]:
● CDSD2015 [24]
● UCL [26]
● UCL [26]
Line intensity (cm/molecule)
1E-25
1E-26
1E-27
1E-28
1E-29
Wavenumber (cm^{-1})
3620
3640
3660
3680
3700
3720
11112e-11101e (636)
○ HITRAN2016 [12]:
● UCL [27]
● CDSD2015 [24]
● CDSD2019 [14]
Line intensity (cm/molecule)
1E-26
1E-27
1E-28
1E-29
1E-30
Wavenumber (cm^{-1})
2040
2060
2080
2100
2120
2140
2160

Fig. 12.

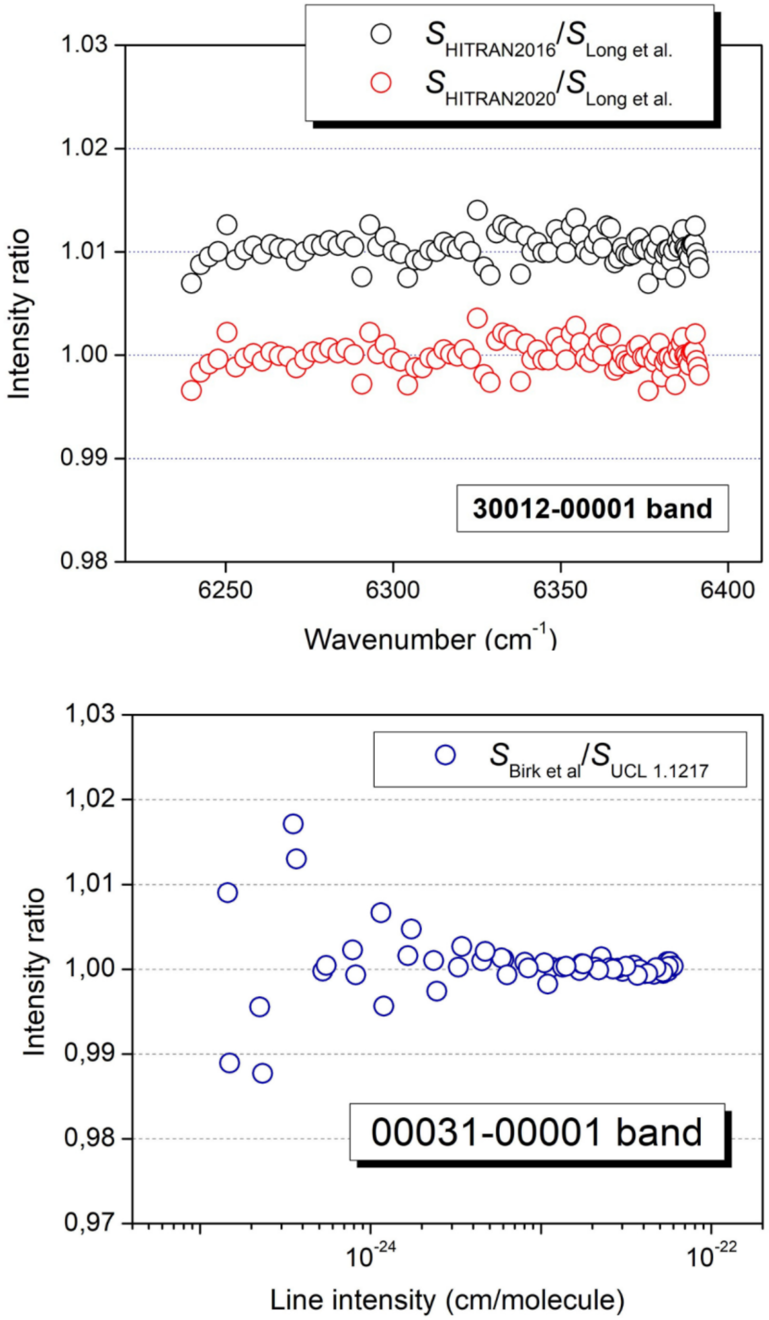
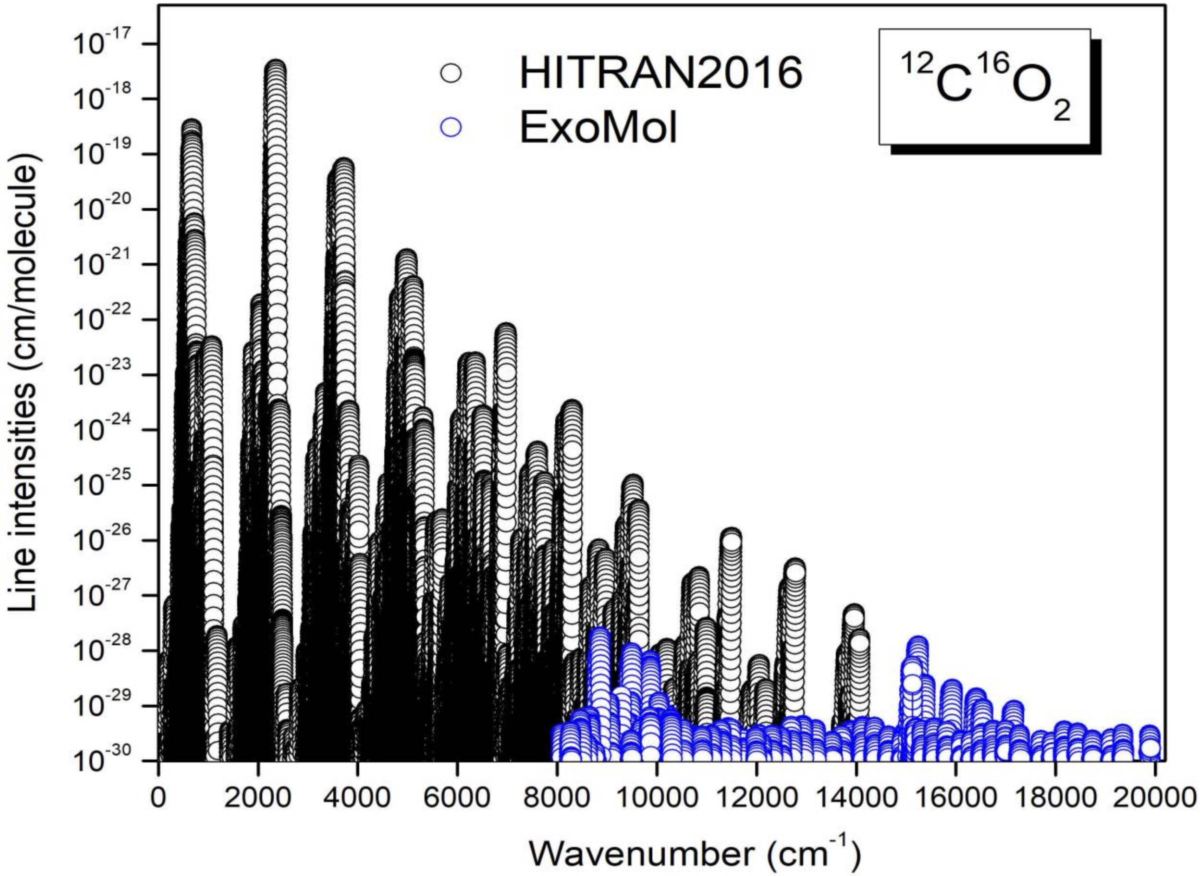

$S_{\mathrm{HITRAN2016}}/S_{\mathrm{Long\ et\ al.}}$
$S_{\mathrm{HITRAN2020}}/S_{\mathrm{Long\ et\ al.}}$
Intensity ratio
1.03
1.02
1.01
1.00
0.99
0.98
30012-00001 band
6250
6300
6350
6400
Wavenumber (cm^{-1})
$S_{\mathrm{Birk\ et\ al}}/S_{\mathrm{UCL\ 1.1217}}$
Intensity ratio
1,03
1,02
1,01
1,00
0,99
0,98
0,97
00031-00001 band
10^{-24}
10^{-22}
Line intensity (cm/molecule)

Fig. 13.



HITRAN2016
ExoMol
$^{12}C^{16}O_2$
Line intensities (cm/molecule)
10^{-17}
10^{-18}
10^{-19}
10^{-20}
10^{-21}
10^{-22}
10^{-23}
10^{-24}
10^{-25}
10^{-26}
10^{-27}
10^{-28}
10^{-29}
10^{-30}
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
Wavenumber (cm^{-1})

Fig. 14.

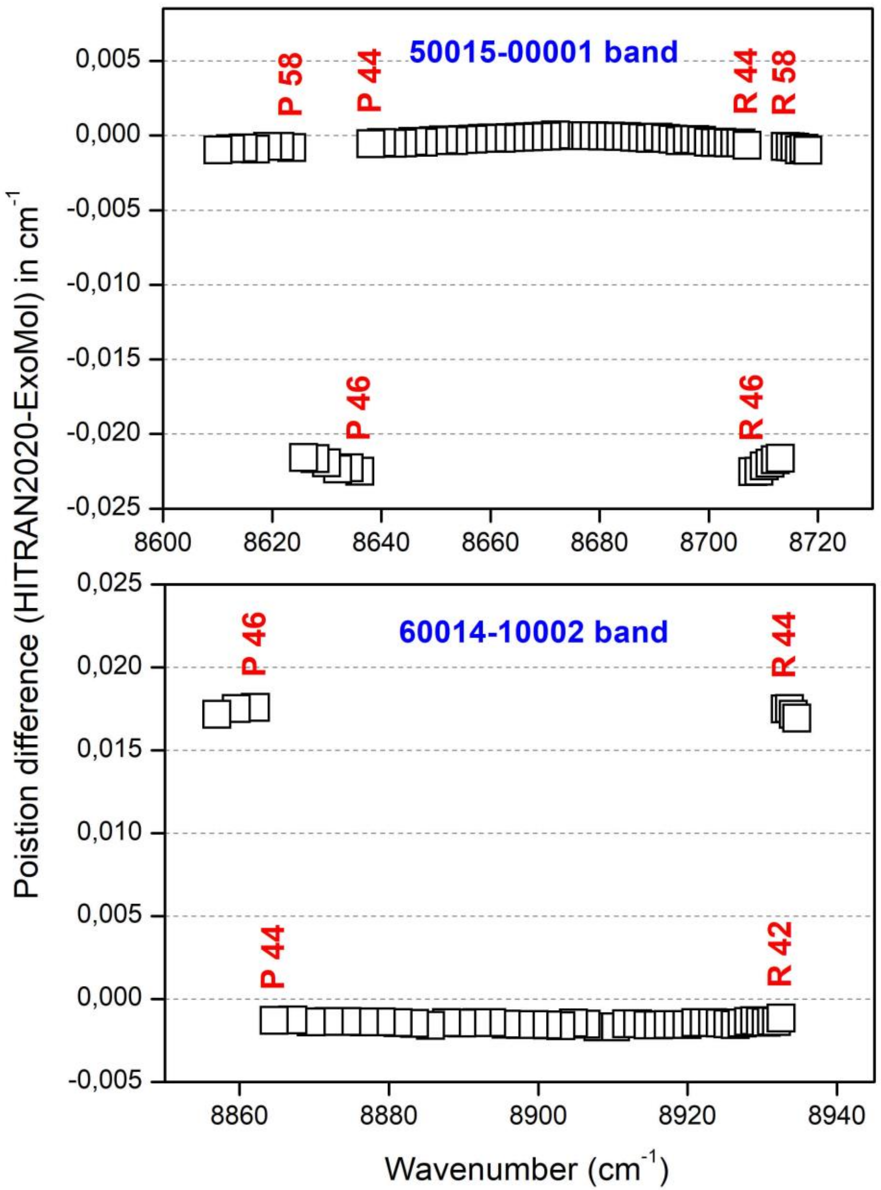
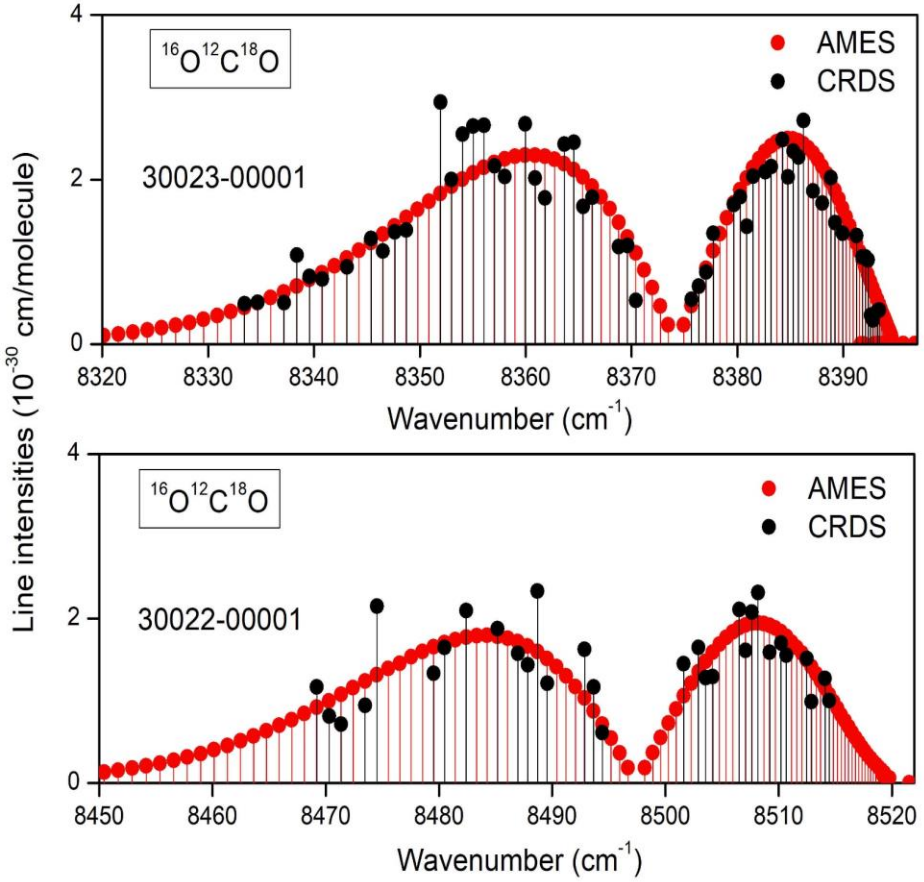
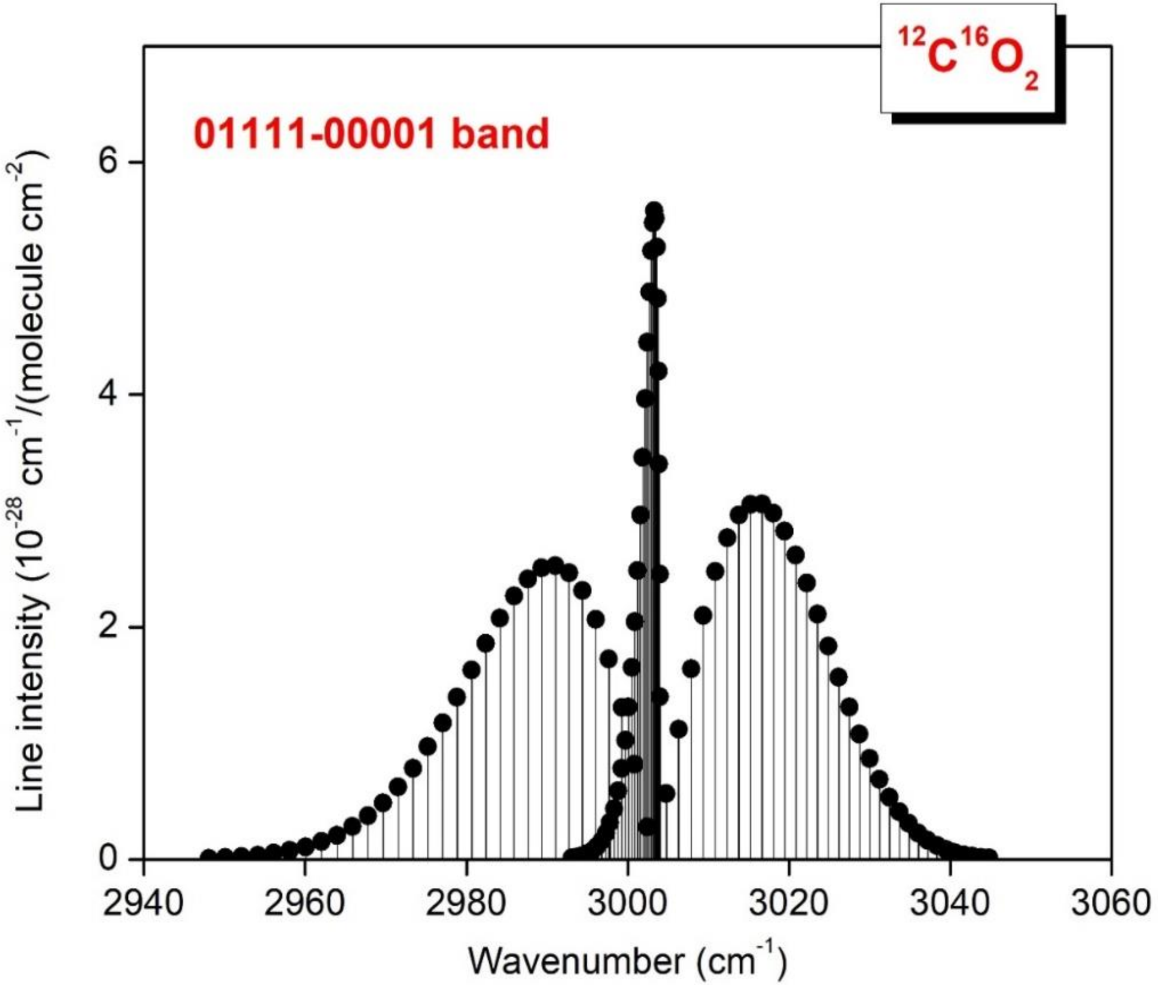

50015-00001 band
P 58
P 44
R 44
R 58
P 46
R 46
0,005
0,000
-0,005
-0,010
-0,015
-0,020
-0,025
8600
8620
8640
8660
8680
8700
8720
60014-10002 band
P 46
R 44
P 44
R 42
0,025
0,020
0,015
0,010
0,005
0,000
-0,005
8860
8880
8900
8920
8940
Poistion difference (HITRAN2020-ExoMol) in cm^{-1}
Wavenumber (cm^{-1})

Fig. 15.



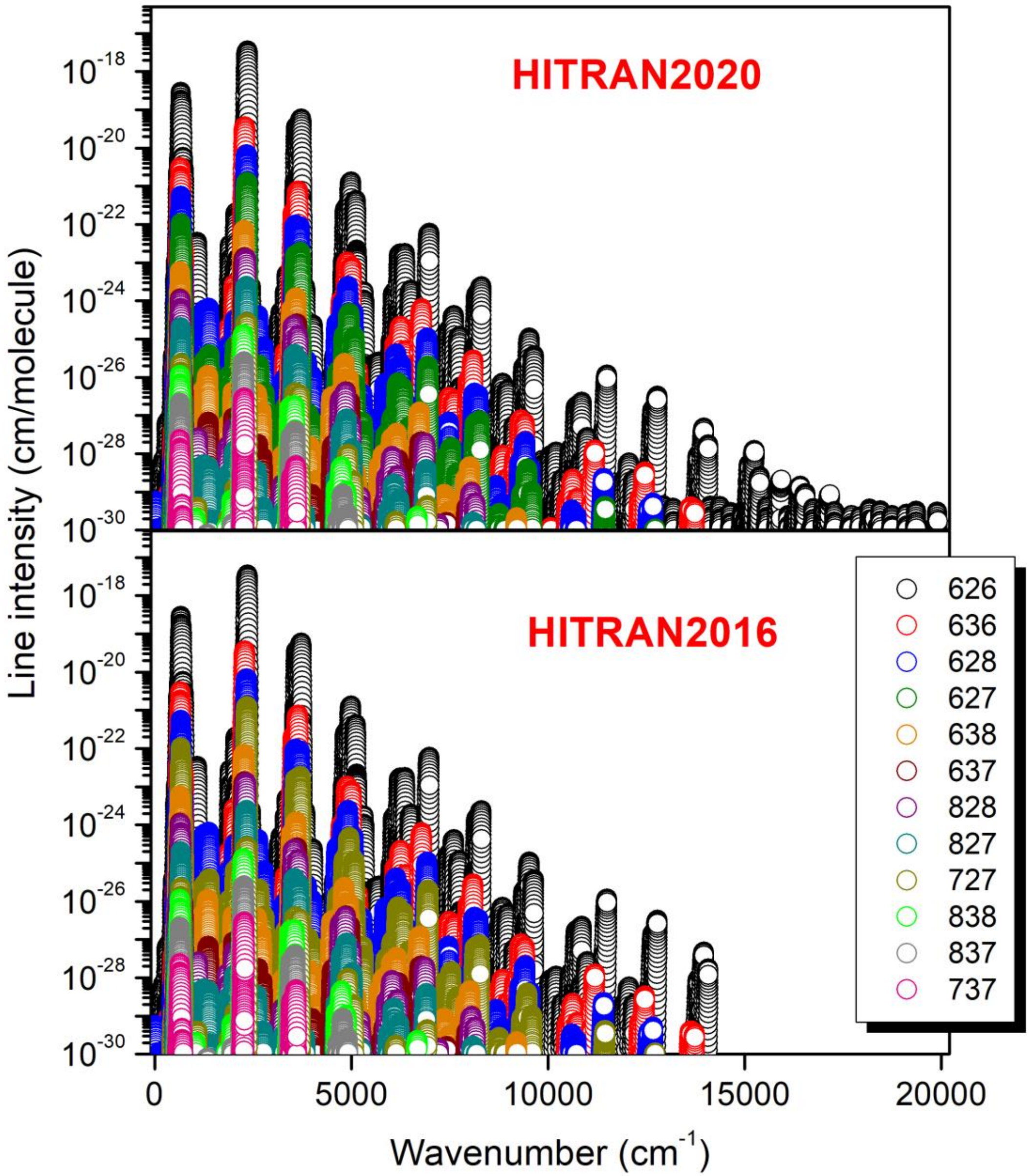
$^{16}O^{12}C^{18}O$
AMES
CRDS
30023-00001
Line intensities (10^{-30} cm/molecule)
0
2
4
8320
8330
8340
8350
8360
8370
8380
8390
Wavenumber (cm^{-1})
$^{16}O^{12}C^{18}O$
AMES
CRDS
30022-00001
0
2
4
8450
8460
8470
8480
8490
8500
8510
8520
Wavenumber (cm^{-1})

Fig. 16.



$^{12}C^{16}O_2$
01111-00001 band
Line intensity (10^{-28} cm^{-1}/(molecule cm^{-2}))
0
2
4
6
2940
2960
2980
3000
3020
3040
3060
Wavenumber (cm^{-1})

Fig. 17.


HITRAN2020
HITRAN2016
Line intensity (cm/molecule)
10^{-18}
10^{-20}
10^{-22}
10^{-24}
10^{-26}
10^{-28}
10^{-30}
0
5000
10000
15000
20000
Wavenumber (cm^{-1})
○ 626
○ 636
○ 628
○ 627
○ 638
○ 637
○ 828
○ 827
○ 727
○ 838
○ 837
○ 737

Declaration of Competing Interest

Author Statement

E.V.Karlovets: Formal analysis, Methodology, Software, Writing - original draft., I.E.Gordon: Supervision, Conceptualization, Methodology, Writing - review & editing, L.S.Rothman: Writing - review & editing, R. Hashemi: Data curation, Writing - review & editing, R.J.Hargreaves: Software, G.C. Toon: Data curation, Software, A.Campargue: Data curation, Writing - review & editing, V.I. Perevalov: Data curation, Writing - review & editing, P. Čermák: Software, M.Birk: Data curation, G.Wagner: Data curation, J.T.Hodges: Data curation, Writing - review & editing, J. Tennyson: Writing - review & editing, S.N.Yurchenko: Data curation, Writing - review & editing.

Supplementary Material